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OUTLINES OF CHEMISTRY,

FOR

THE USE OF STUDENTS.

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OUTLINES OF CHEMISTRY,

For the Use of Students.

BY

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PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF EDINBURGH.

WITH ENGRAVINGS ON WOOD.

PART II.—ORGANIC CHEMISTRY.

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PREFACE TO PART II.

The Outlines of Organic Chemistry, on the same plan as the Outlines of Inorganic Chemistry, are now offered to the public.

In the present state of Organic Chemistry, a complete and scientific arrangement is quite unattainable, and I have therefore followed, in most points, the order adopted by Professor Liebig and myself in the last editions of Turner's "Elements of Chemistry." This arrangement is so far convenient that substances of analogous properties and composition are treated of together; but it is only in the case of the known or admitted organic radicals that it is at all systematic.

With regard to the disputed question of the existence of organic radicals, I wish to be understood as only availing myself of the view which admits them for the purpose of aiding the memory in recollecting and associating the vast number of facts already established in Organic Chemistry. For this purpose, the theory of compound radicals, wherever it can be applied with some probability, has very great advantages; but I am fully aware how probable it is that our views in reference to the greater number of admitted radicals must, ere long, be very considerably modified. Still, it must not be forgotten, that we have obtained several radicals, as, for example, *cyanogen* and ***kakodyle***, in the separate state, and that in these cases all analogy confirms the theory in question, according to which cyanogen is a compound radical, ranking with the simple unmetallic radicals, chlorine, iodine, &c., while kakodyle is a compound radical, possessed of all the chemical characters and relations of the simple metals.

The remainder of the arrangement, after the admitted radicals have been considered, is entirely empirical, bodies being classed according to their properties, as acids, oils, colouring matters, bases, nutritious matters, products of destructive distillation, and so on. Having made both the Table of Contents and the Index very full, I trust that reference to the very numerous individual substances mentioned will be found easy.

The recent progress of Organic Chemistry has been, and still continues to be, so astonishingly rapid, that it has been necessary to rewrite several sections; and there is no section to which additions have not been made since they were first written.

In fact, Organic Chemistry is, at present, not only in a state of rapid development and progress,* but in a state of transition; for every Chemist feels, that he cannot remain satisfied with the views at present held.

Two very distinguished French Chemists, M. Laurent and M. Gerhardt, have lately given to the world new systems of classification for the known organic compounds and their derivatives. Both systems are in the highest degree ingenious, and will certainly have a powerful effect in hastening the progress of the science. I have not, however, alluded in this work to these systems, because they are as yet incomplete, only the first volume of M. Gerhardt's "Précis de Chimie Organique" having yet appeared, while the views of M. Laurent have not yet been published except in the form of memoirs and abstracts of memoirs read before the Academy. To all those who wish to pursue the subject farther than this little work extends, I would cordially recommend the study of the recent writings of the two chemists just mentioned, both of whom have made very great additions to our knowledge by their researches. Indeed, for the extent and accuracy of his researches, as well as the originality and profundity of his views, M. Laurent has long been unrivalled in France, a country so fertile in distinguished Chemists; and he is unquestionably the original author of those views, especially in reference to chemical types and substitution, or metalepsy, as it is now called, which are now prevalent in France and generally admitted elsewhere.

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* As a proof of the rapid progress of the science, I may mention, that, since the printing of the section on the bile, in the penultimate sheet of this part, I have seen it stated, that my friend Professor Redtenbacher, of Prague, has discovered that Taurine (see p. 545) contains 26 per cent. of *sulphur*, hitherto overlooked. Should this be confirmed, then choleic acid and bile must also contain much sulphur, and in that case some views now held must necessarily be much modified.—*See* ADDENDA, p. 568.

I would also recommend to the reader, if desirous to pursue the subject, the lectures of Professor Liebig on Organic Chemistry, published in the "Lancet," which will soon, I trust, be resumed, as well as the works of the same author on the application of Chemistry to Agriculture and to Physiology. To these works, indeed, the present Outlines are intended, in some measure, to serve as an introduction. Finally, the admirable work of Professor Mulder, of Utrecht, on Physiological Chemistry, the first part of which has already appeared in English, ought to be carefully studied. The very extensive and varied researches of Professor Mulder, distinguished as they are for accuracy, have conferred on him a very high position among the cultivators of Organic Chemistry.

Into the disputed questions of Physiological Chemistry I have hardly entered, and have confined myself to a very brief account of what is best known on these points. The reader who wishes to follow out this part of the subject must consult the works of Liebig, of Dumas and Boussingault, of Johnston and of Mulder.

For the extreme brevity of these Outlines, which are chiefly intended as a text-book for my own lectures, and for their many imperfections, of which no one is more sensible than I am, I beg now to apologise, pleading the immense extent of the subject, and the necessity of keeping within certain narrow limits, with a view to the usefulness of the work for students. At the same time I cannot refrain from expressing my gratitude for the very favourable reception given to the first part of these Outlines.

WILLIAM GREGORY.

University of Edinburgh,
June 2nd, 1845.

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OUTLINES OF CHEMISTRY.

PART II.

R

ORGANIC CHEMISTRY.

INTRODUCTORY.

Organic Chemistry is so called because it treats of the substances which form the structure of organised beings, and of their products, whether animal or vegetable. It has long been known, that all organised structures, as well as all the substances formed in or by these, are, in great part, composed of a very limited number of elements; insomuch that a large proportion of them may be described as consisting, almost exclusively, of only four simple substances, namely, Carbon, Hydrogen, Oxygen, and Nitrogen.

But while these four elements undoubtedly constitute the chief part of all organised tissues, and while such products as woody fibre, sugar, starch, gum, fat, oils, and many organic acids, contain only the first three, that is, Carbon, Hydrogen and Oxygen, we must not forget that other elements occur in the organised kingdoms of nature; some of them, such as those of Phosphate of Lime, in large quantity; and all, whether they occur in smaller or greater proportion, as truly essential to animal and vegetable life, as the four elements above mentioned, the predominance of which characterises the organic world.

Thus, no plant can grow, or form cells, or even fibre, without the presence of certain mineral or saline compounds, which are derived from the soil, and which when the plant is burned, constitute its ashes. These are, Potash, Soda, Lime, Magnesia, with, occasionally, oxides of Iron and Manganese, as bases; and Silicic Acid, Phosphoric Acid, Sulphuric Acid, Chlorine and Fluorine, as acids and acid-radicals.

Again, the juices of all plants, and more especially their roots and seeds, contain some one or more of the compounds known by the names of albumen, fibrine, and caseine. Now these compounds contain small, but absolutely essential proportions of sulphur and phosphorus, besides earthy and alkaline phosphates.

Lastly, the bones of animals contain not only phosphate of lime, but also phosphate of magnesia and fluoride of calcium, both in very considerable quantity; and Iron is an unfailing constituent of blood.

To the four elements first mentioned, as constituting the chief mass of organic substances, we must therefore add, as no less essential, although for the most part in smaller proportion, the following metalloids, Chlorine, Fluorine, Sulphur, Phosphorus, and Silicon; and the following metals, Potassium, Sodium, Calcium, Magnesium, Iron, and occasionally Manganese.

It thus appears that the fourteen or fifteen elements which constitute the chief mass of the mineral or inorganic world, are almost the same which occur in organised matter: the difference being chiefly this, that in inorganic nature the *predominant* elements, nearly in the order of their abundance, are, Oxygen, Hydrogen, Nitrogen, Silicon, Chlorine, Sodium, Aluminum, Carbon, and Iron, after which follow Potassium, Calcium, Magnesium, Sulphur, Phosphorus, and Fluorine; while in the organic department the order is nearly as follows, Carbon, Oxygen, Hydrogen, Nitrogen, Potassium, Calcium, Phosphorus, Silicon, Sulphur, Sodium, Magnesium, Chlorine, Iron, and Fluorine. Aluminum, so very abundant in the mineral kingdom, hardly ever occurs in organic compounds, and when it does occur, is perhaps accidental.

The above considerations are sufficient to show, that there is no essential distinction to be made between organic and inorganic Chemistry, founded on the nature of the elements concerned.

Neither is there any such distinction to be pointed out in regard to the laws of combination and decomposition which prevail in these different departments of chemistry; for we find the same affinities operating; and although organised tissues, and their products, have, in general, a more complicated constitution than inorganic compounds, containing a larger number of equivalents of their elements, and consequently having much higher atomic weights, we cannot consider such characters as forming a valid ground of distinction.

But while we should find it very difficult, if not impossible, to draw the line between inorganic and organic Chemistry on scientific principles, we may still recognise, for convenience sake, a certain distinction, founded, first, on the origin of substances, whether animal and vegetable, or mineral; and secondly, on the uniform predominance of carbon in animal and vegetable matter.

In reference to the first point, it is to be observed, that, although the elements concerned are those common to the inorganic and organic kingdoms, the compounds which constitute the latter are formed under peculiar circumstances, such as, for the most part, cannot be imitated in our experiments.

It is true that chemistry has succeeded, in some cases, in forming artificially certain compounds which occur as products of organic life, such as Urea, Formic Acid, and Oil of Spiræa. But, in the first place, most, if not all of these, require for their production the aid of an organic product: thus, Formic Acid is produced from Starch, Oil of Spiræa from Salicine; and although Urea may be obtained from Cyanic Acid and Ammonia, it is doubtful if either Cyanogen or Ammonia can be obtained except from organic compounds, directly or indirectly. Secondly, it is particularly to be noticed, that we have not yet succeeded in forming, artificially, either an organised tissue, or even any one of the compounds (albumen, &c.) of which such tissues are made. Those organic compounds which have been artificially formed, are invariably *products of decomposition*, or, in other words, the excretions or secretions of organised bodies; and are far less complex in their constitution than organised structures.

From these facts we draw the conclusion, that certain circumstances, of which the most important is the *vital force*, so modify the play of affinities in organised beings, as to produce the compounds usually termed organic, which, so far as they are capable of entering into the composition of tissues, cannot be imitated by art.

In regard to the second peculiarity of organic compounds, namely, the predominance of carbon in their composition, we observe that, as this carbon is united to the three gases, Oxygen, Hydrogen, and Nitrogen, with each of which it forms gaseous compounds, and as, further, the latter elements, among themselves, form compounds, such as water and ammonia, which are also volatile, so the action of heat on organic compounds is characteristic; producing *combustion* of all, save the ashes, when there is free access of air; and *charring* them, or, in other words, causing the separation of part of their carbon, in close vessels, while the greater part is dissipated in the form of volatile products.

Here, then, we have a ready test of organic matter, which is so characteristic, that we might almost define Organic Chemistry as the Chemistry of such compounds as are charred when heated to redness in close vessels. There are very few substances, indeed, of organic origin, which do not exhibit this character.

Organic Chemistry has been defined as the Chemistry of Compound Radicals; but, although we must admit the existence of many such radicals in Organic Chemistry, we cannot adopt this definition in contradistinction to that of Inorganic Chemistry, as the Chemistry of Simple Radicals, because the recent progress of science has led, or almost compelled us to admit the existence of compound radicals in Inorganic Chemistry, as has been explained in the first Part of this work.

It is, perhaps, worth while to point out, that all the organic compound radicals hitherto established, or supposed to exist, are compounds of carbon, if we except amidogen (see p. 64), which contains only hydrogen and nitrogen.

It is also proper here to state, that, under the name of organic compounds, many substances are treated of which do not occur in nature, but which have been obtained by subjecting true organic products to various influences: to that, for example, of heat, as in what is called the destructive distillation, which yields such substances as naphtha, naphthaline, &c.; or to the action of chlorine or bromine, of sulphuric or nitric acids, of alkalies, &c., by all which means whole series of new compounds are obtained. Lastly, some very interesting and important compounds are included under the term organic, which arise from the addition of elements not naturally occurring in the organic kingdom; as for example, kakodyle and its compounds, which contain arsenic as an essential constituent; and the very singular bases in which platinum is added to the usual elements of organic alkalies.

But while, as has just been stated, compound radicals are not exclusively characteristic of organic chemistry, we may still derive great assistance from attending to the compound radicals of organic chemistry. For while we admit the existence of such radicals in inorganic chemistry, along with simple radicals, we must bear in mind that all the organic radicals as yet discovered are compound, and many of them exceedingly complex, containing three or four elements.

It is true that we are not yet acquainted with the radicals of a very large proportion of organic compounds; such as the principal organic acids, the organic alkalies, &c. But the known organic radicals furnish us with the means of classifying many most important substances, just as we classify the compounds of any metalloid or of any metal together. As to those groups or series of organic compounds, the radicals of which are not yet known, we can only class them according to analogies of properties, of composition, or of both.

With these introductory remarks, we shall proceed to consider the known organic compound radicals, and their derivatives.

COMPOUND ORGANIC RADICALS.

A compound radical is a substance which, although containing two or more elements, enters into combination with elementary bodies as if it were itself elementary, and in ordinary circumstances performs exactly the part of an element.

In the first part of this work, we have already admitted as probable the existence of inorganic compound radicals, such as

SO_4, the radical of sulphuric acid, and NO_6, that of nitric acid. These bodies are, in their relations to others, entirely analogous to chlorine. Thus we may represent the acids of these three radicals, with their potassium and silver salts as follows :—

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine	$H + Cl$	$K + Cl$	$Ag + Cl$
	SO_4	$H + SO_4$	$K + SO_4$	$Ag + SO_4$
	NO_6	$H + NO_6$	$K + NO_6$	$Ag + NO_6$

The compound inorganic radicals, SO_4 and NO_6, therefore, perform exactly the part of a metalloid of the group of chlorine.

But there have also been briefly mentioned, in the first Part, certain compound organic radicals, which not only exhibit, in their relations, characters analogous to those of chlorine, but actually exist, like chlorine, in the separate state, which is not the case with SO_4 and NO_6, these latter being only known in combination.

The organic radicals here alluded to are Cyanogen, $C_2N = Cy$, and Mellone $C_6N_4 = Me$ (see Part I., p. 121). They may be compared to chlorine exactly like the two above mentioned inorganic compound radicals. Thus,

		Acid.	Potassium Salt.	Silver Salt.
Radicals	Chlorine Cl	$H + Cl$	$K + Cl$	$Ag + Cl$
	Cyanogen Cy	$H + Cy$	$K + Cy$	$Ag + Cy$
	Mellone Me	$H + Me$	$K + Me$	$Ag + Me$

Cyanogen and Mellone are, therefore, radicals of the nature of the chlorine group of metalloids. The bisulphuret of cyanogen, or sulphocyanogen, $C_2NS_2 = CyS_2$, although it contains three elements, plays the same part as chlorine or cyanogen, and forms with hydrogen the acid $H + CyS_2$, and with potassium the salt $K + CyS_2$.

Some compound organic radicals appear more analogous to the combustible group of metalloids, that is, to carbon, sulphur, or phosphorus ; inasmuch as they form acids with oxygen, or rather with the elements of water like those metalloids, and are besides capable of entering into combination with chlorine, iodine, &c. Such radicals are carbonic oxide, CO, or rather an isomeric modification of it, C_2O_2; acetyle, C_4H_3; and formyle, C_2H. Each of these may be viewed as the radical of a powerful acid ;

for $C_2 O_2 + O = C_2 O_3$ is dry oxalic acid; $C_4 H_3 + O_3$ is dry acetic acid; and $C_2 H + O_3$ is dry formic acid. Again, the first forms with chlorine the compound $C_2 O_2 + Cl_2$, called phosgene gas or chlorocarbonic acid, while the two others yield $C_4 H_3 + Cl$, the chloride of acetyle, and $C_2 H + Cl_3$, the perchloride of formyle.

Further, there are organic compound radicals which play the part of metals, forming salts with chlorine, iodine, sulphur, cyanogen, &c., and yielding, with oxygen, compounds possessing basic properties analogous to those of metallic oxides. Such radicals are ethyle, $C_4 H_5$, methyle, $C_2 H_3$, and kakodyle, $C_4 H_6 As_2$.

Radicals.	Oxygen Compound.	Chlorine Compound.	Cyanogen Compound.	Sulphur Compound.
Ethyle $C_4 H_5 = Ae$	Ae O	Ae Cl	Ae Cy	Ae S
Methyle $C_2 H_3 = Mt$	Mt O	Mt Cl	Mt Cy	Mt S
Kakodyle $C_4 H_6 As_2 = Kd$	Kd O	Kd Cl	Kd Cy	Kd S

Lastly, there are some compound organic radicals, which partake of the characters of the two last groups, forming, like the acetyle group, acids and not bases with oxygen; but yielding, with chlorine, sulphur, cyanogen, &c., compounds analogous to those formed by the ethyle group. To this division belong Benzoyle, $C_{14} H_5 O_2 = Bz$; Cinnamyle, $C_{18} H_8 O_2 = Ci$; and several others. Benzoyle and cinnamyle, with the addition of oxygen and the elements of water, produce benzoic acid, BzO, HO, and cinnamic acid, Ci O, HO. This group is characterised by forming with hydrogen certain essential oils. Thus, benzyle yields, with hydrogen, the essential oil of bitter almonds, Bz H; cinnamile yields the oil of cinnamon, Ci H; and salicyle, $C_{14} H_5 O_4 = Sa$, another radical of this group, forms, with hydrogen, the oil of spiræa, Sa H.

These brief statements will serve to show that there are different kinds or groups of compound radicals, just as there are of simple ones; and further, that these compound radicals exhibit a very remarkable tendency to combine with simple radicals, and, in fact, to act the part of elementary bodies. And let us here bear in mind that the only real difference, in this point of view, between cyanogen and chlorine is this, that in the case of the former we can prove the radical to be compound, while we cannot as yet do this in the case of the latter. But, as formerly pointed out, we call chlorine, and indeed all other elements simple, only because we have not been able to show them to be compound; without having any certainty that they are really and absolutely simple. If we could not resolve cyanogen into carbon and nitrogen, we should be compelled to add it to the list of elements.

But although compound radicals usually act towards other bodies as if simple, and consequently combine generally with simple substances, they are also capable of uniting with each other. In fact, this is but another proof of their close resemblance to elementary bodies in their relations; for as simple metals, such as potassium and silver, unite with cyanogen just as with chlorine, so also such compound radicals as are analogous to metals can combine with cyanogen, itself a compound radical. Thus ethyle, methyle, benzoyle, and kakodyle all combine with cyanogen, yielding compounds formed of two organic radicals, one playing the part of a metalloid, the other that of a metal.

Compounds of this nature furnish the very best proof and illustration of the advantages which we derive from the doctrine of compound radicals, acting like elements, whenever we are justified by facts in adopting and applying it. Thus a compound has been formed by the mutual action of a compound of kakodyle and a compound of cyanogen, the analysis of which proves that it contains carbon, hydrogen, nitrogen, and arsenic, in the relative proportions indicated by the formula $C_6\,H_6\,N\,As_2$. What view are we to take of such a formula? and if we look on the compound as one formed of these four elements indiscriminately united, how are we to retain such an isolated fact in the memory? But if, on the other hand, we view it as the cyanide of kakodyle, $= C_4\,H_6\,As_2 + C_2\,N$, or, using the abbreviated notation appropriate to compound radicals, Kd Cy, we are at once enabled to retain the composition and chemical relations of the compound. Moreover, when we find that the radical, Kd ($=C_4\,H_6\,As_2$) exists in a separate form, and that it forms, with oxygen, two compounds, Kd O and Kd O_3; with chlorine, Kd Cl; with sulphur, Kd S; and that, in short, it plays the part of a metal in all its compounds, and may in fact be separated from some of these by metals having stronger affinities than itself, we are supplied with an idea which serves to connect and to fix all these and many more analogous facts in the memory.

When we further observe, to pursue the same example, that the cyanide of kakodyle, Kd Cy, when acted on by hydrochloric acid, gives rise to hydrocyanic acid and chloride of kakodyle; and that, when acted on by potash, it yields cyanide of potassium and oxide of kakodyle, we acquire so many additional proofs of the entire analogy between simple and compound radicals in their relations to other bodies. For the two changes or reactions above-mentioned are expressed by the equations, $Kd\,Cy + H\,Cl = Kd\,Cl + H\,Cy$; and $Kd\,Cy + K\,O = Kd\,O + K\,Cy$; and these equations are exactly similar to those which occur most frequently in inorganic chemistry.

The facts already ascertained with regard to those compound organic radicals, whose existence has been either established, or rendered highly probable, entitle us to conclude that all organic compounds contain one or more organic radicals, combined either with each other, or with elementary radicals. In studying, therefore, any organic product, one chief object is to determine what organic radical or radicals it contains, since the knowledge of these at once gives us a means of classification.

Thus alcohol, on the theory of compound radicals, is considered as the hydrated oxide of ethyle; ethyle being an organic radical, C_4H_5. So that alcohol, $C_4H_6O_2$ is more accurately represented as $(C_4H_5)\,O + H\,O$; or, if we represent ethyle, C_4H_5, by Ae, then alcohol becomes $Ae\,O, H\,O$, hydrated oxide of ethyle; perfectly analogous to $K\,O, Ho$, hydrated oxide of potassium, or caustic potash.

Again, benzoic ether, $C_{18}H_{10}O_4$, is viewed as benzoate of oxide of ethyle, $C_4H_5O + C_{14}H_5O_3$; or, more briefly, $Ae\,O + Bz\,O$. Here we have the basic oxide of one radical united with the acid oxide of another.

It is very often by means of thus tracing the different organic radicals, that we are enabled to explain the very numerous cases of isomerism, which occur in organic chemistry. Thus, the following compounds have the same composition in 100 parts:—

Aldehyde	$C_4H_4O_2$
Acetic Ether	$C_8H_8O_4$
Butyric Acid . . .	$C_8H_8O_4$

Now, aldehyde is considered to be the hydrated protoxide of acetyle, $(C_4H_3)\,O + H\,O$; or, abbreviated, $Ac\,O, H\,O$. Again, acetic ether is acetate of oxide of ethule, $C_4H_5O + (C_4H_3)\,O_3$; or, shortly, $Ae\,O, Ac\,O_3$; the dry acetic acid, $Ac\,O_3 = (C_4H_3)\,O_3$, being a peroxide of the same radical, acetyle, $(C_4H_3 = Ac)$ of which aldehyde is the protoxide. Lastly, butyric acid is considered (on the older view of acids,) as a hydrated acid, a compound of water with dry butyric acid; thus, $H\,O + C_8H_7O_3$. It is true, that in the latter case, we are not yet acquainted with the true radical of butyric acid; but, we cannot doubt that, like acetic acid, it does contain a radical. These three compounds, therefore, may now be represented and distinguished as follows:—

	Empirical Formula.		Rational Formula.
Aldehyde. .	$C_4H_4O_2$	=	$(C_4H_3)\ O + HO$
Acetic Ether	$C_8H_8O_4$	=	$(C_4H_5)\ O + (C_4H_3)\ O_3$
Butyric Acid	$C_8H_8O_4$	=	$C_8H_7O_3 + HO$

Even in those cases in which the composition of the radical is not known, or not known with certainty, we can often trace the radical with much probability. Thus, dry oxalic acid, C_2O_3, and dry mellitic acid, C_4O_3, may be viewed as different compounds of the simple radical carbon, the latter containing just twice the proportion of carbon to the same quantity of oxygen that the former does. This is merely stated by way of illustration: for, it is at least equally probable that the true radical of oxalic acid is C_2O_2.

But in the following four acids we may trace, theoretically, the same compound radical, namely, formyle, $= C_2H$, in combination with different proportions of oxygen. Here C_2H is also represented by Fo.

Formic Acid	$(C_2H) + O_3 = Fo\,O_3$	
Succinic Acid	$C_4H_2O_3 = 2\ (C_2H) + O_3$	$= Fo_2\,O_3$
Malic Acid	$C_4H_2O_4 = 2\ (C_2H) + O_4$	$= Fo_2\,O_4$
Racemic Acid	$C_4H_2O_5 = 2\ (C_2H) + O_5$	$= Fo_2\,O_5$

These relations, although as yet only to be traced in the formulæ, are yet not without interest, and may, at all events, serve to aid the memory.

In like manner, it may be observed, that the following acids all contain, as hydrates, 4 eq. of oxygen; and all likewise the same number of eqs. of carbon as of hydrogen.

Acetic Acid	=	$C_4\ H_4\ O_4$
Butyric Acid	=	$C_8\ H_8\ O_4$
Valerianic Acid	=	$C_{10}\ H_{10}\ O_4$
Œnanthic Acid	=	$C_{14}\ H_{14}\ O_4$
Lauric Acid	=	$C_{24}\ H_{24}\ O_4$
Cocinic Acid	=	$C_{26}\ H_{26}\ O_4$
Ethalic Acid	=	$C_{32}\ H_{32}\ O_4$
Margaric Acid	=	$C_{34}\ H_{34}\ O_4$

Here we may suppose the radical of the first acid to have been changed by the successive additions of 4, 6, 10, or 20 eqs. of carbon and hydrogen, the oxygen remaining unchanged. Or we may as readily suppose one of these acids, by losing oxygen, to pass into another. Thus we may either conceive butyric acid to be formed from acetic acid by the addition of C_4H_4; or acetic acid to give rise to butyric acid, by losing half its oxygen; for $2\ (C_4H_4O_4) = C_8H_8O_8$; and $C_8H_8O_8 - O_4 = C_8H_8O_4$.

When compound organic radicals, or their compounds, are subjected to powerful decomposing agencies, they tend to produce new and less complex radicals. Thus, when alcohol, the hydrated oxide of ethule, is oxidised, it gives rise to aldehyde and acetic acid, which are compounds of acetyle, $C_4 H_3$, a less complex radical than ethyle, $C_4 H_5$. Further, when organic compounds are decomposed by a strong heat, they tend to produce compounds of simple radicals, such as carbon or hydrogen, or, at most, of the least complex radicals, such as cyanogen, $C_2 N$, and amidogen, $N H_2$. These are principles of very general application.

It may here be observed, that while, in such cases as the supposed conversion of acetic into butyric acid, by the loss of half its oxygen, the change is from a less complex to a more complex organic compound, and while we can hardly doubt the possibility of such a result, yet the oxidation of a compound radical, that is, the addition of oxygen, appears always to produce less complex radicals or compounds.

It is often urged, as an argument against the doctrine of compound radicals, that these supposed radicals are entirely imaginary, and cannot be produced. Now, it is true, that a large proportion of those, whose existence is best attested, have not yet been obtained in the uncombined state; and it is even probable that some of them are only capable of existing, or rather of being preserved, when combined. But the argument founded on this fact has no cogency; for, in the first place, some organic radicals, such as cyanogen and kakodyle, are well known in the separate state. Now cyanogen and kakodyle are, in all their relations, exactly analogous, the former to chlorine, the latter to a metal; and, if we were unable to demonstrate their compound nature, their chemical relations would compel us to classify cyanogen as an element along with chlorine, and kakodyle along with the metals; and when we see whole series of organic compounds, in all respects analogous to those of cyanogen and kakodyle, we are entitled logically to draw the conclusion that these compounds contain similar compound radicals, even although we cannot isolate them. Secondly, in every chemical theory yet broached, many substances are admitted whose existence cannot be directly proved. Thus, the so-called anhydrous organic acids are, almost without exception, unknown in the separate state; they are equally imaginary with the radicals whose existence is doubted. Nay, many inorganic acids are equally hypothetical. Anhydrous nitric acid has never been seen; and, although there are reasons for doubting its existence, yet no one doubts the existence of hyposulphurous acid, which yet has never been separated, either as a hydrate, or in the anhydrous state.

We conclude, therefore, that organic compound radicals exist, and generally play the part of elements; and we shall avail ourselves of their existence, as far as it is are established, to facilitate the study, the classification, and the retention in the memory, of organic compounds.

THEORY OF CHEMICAL TYPES.—DOCTRINE OF SUBSTITUTION.

The original and ingenious researches of Laurent have led to the adoption of what is called the Theory of Types and the Law or Doctrine of Substitution, which have been supported, and in a great measure established, by Dumas and other distinguished experimenters of the French school. The views of Laurent and of Dumas were, for a time, vehemently opposed by some chemists, especially by Berzelius and Liebig; but although they have in some points been modified and restricted, the progress of discovery has gradually led to their general reception, so that recently some of the most striking illustrations and proofs of the law of substitution have been discovered by Dr. Hoffman, assistant to Professor Liebig, and working under his eye.

As the subject, therefore, is no longer purely controversial, it would be wrong to omit it from an elementary work, more especially as the doctrine has now taken such a form as to facilitate very much the study of organic compounds and of their metamorphoses.

It is not easy to define a chemical type; but in inorganic chemistry we may say, for example, that hydrochloric acid, $H\,Cl$, is the type of a very numerous class of acids, the character of which is that they contain hydrogen united to a salt radical.

If for chlorine we substitute iodine, bromine, &c., or even cyanogen, the type remains unchanged, the compound is still an acid, analogous to that which was selected as the type.

Again, common salt, $Na\,Cl$, is the type of a very large series of salts, in which a metal is united with a salt radical; and if we substitute potassium, lead, or silver for the sodium, the type is unaltered; we obtain a different salt, but still a salt of the type represented by $Na\,Cl$.

Here, then, we have the simplest types and the most obvious cases of substitution; when iodine or cyanogen is substituted for chlorine in the acid type; or when potassium, lead, or silver is substituted for sodium in the salt type; in both cases without the loss of the type.

Nay in the salt type, represented by $Na\,Cl$, we may not only replace sodium by other metals, but we may also substitute iodine, bromine, &c., or cyanogen for the chlorine, and still the type will remain unchanged. Iodide of sodium, $Na\,I$, bromide of magnesium, $Mg\,Br$. and cyanide of silver, $Ag\,Cy$, are all as good examples of the salt type represented by $Na\,Cl$, as common salt itself is.

It has been proposed, with great propriety, by Baudrimont, to employ certain Greek characters as symbols in representing the formulæ of extensive types or of types in general. I shall, therefore, express the above salt type by the formula ΔX, in which Δ stands for any metal or body acting as a metal, and X for chlorine or any other radical of analogous power, such as cyanogen. As hydrogen appears to stand alone in the power of forming acids with bodies of the type X, the acid type above alluded to becomes, in its most general form, $H\,X$.

But while it is very easy to understand the extensive substitutions which may be effected in the case of both elements of the type ΔX, yet we observe that in these substitutions the electrical character of the elements is retained; and that as Δ is the positive, and X is the negative element, so they are only replaced, Δ by positive and X by negative elements respectively.

So far as inorganic chemistry is concerned, the study of types would serve generally to confirm and establish the electro-chemical theory. At all events, we are not as yet acquainted with many exceptions to it; we do not usually find oxygen or chlorine occupying the place of Δ in a compound, or a metal playing the part of X. Even in inorganic chemistry, however, there are some examples of such interchanges. Manganese in manganic acid, $Mn\,O_3$, and chromium in chromic acid, $Cr\,O_3$, obviously represent the sulphur in sulphuric acid; and the manganese in hypermanganic acid, $Mn_2\,O_7$ represents the chlorine in perchloric acid, $Cl\,O_7$; while, in its other compounds, manganese acts as a metal.

But the researches of Laurent and Dumas have shown that in organic chemistry the substitution of one element for another, even where the type is retained, is not limited by the electrical character of the elements. Thus, in acetic acid, $H\,O,\ C_4H_3O_3$, the 3 eq. of hydrogen in the anhydrous acid may be replaced by chlorine, giving rise to the compound $H\,O,\ C_4Cl_3O_3$, in which the type is so little affected, that this substance, chloracetic acid, has properties highly analogous to those of acetic acid. Here it is evident that the chlorine performs the same function as the hydrogen which it replaces did; and not, as in hydrochloric acid, an opposite function.

Again, in aldehyde, $(C_4H_3)\,O + H\,O$, the 3 eq. of hydrogen in the radical C_4H_3 may be replaced by 3 eq. of chlorine, and we then have chloral, $(C_4Cl_3)\,O + H\,O$, a body of the same type as aldehyde.

Such cases of substitution of chlorine (iodine, bromine, &c.,)

for hydrogen, and even of oxygen for hydrogen, without change of type, are very frequent ; and it is this kind of substitution, so adverse to the electro-chemical theory, which is included in the theory of substitutions of Laurent. Those more usual substitutions, where one body is replaced by another of similar electric character, may be viewed as so many examples of the doctrine of equivalents, the replacing body being equivalent to that for which it is substituted, on the electro-chemical theory.

Adopting, then, the views of Laurent, we are compelled to admit that the electro-chemical theory fails when applied to cases of substitution of chlorine for hydrogen, &c., where the type remains unaltered. This is clearly the case in acetic and chloracetic acids ; and Hoffman has recently shown that in certain basic organic compounds, hydrogen may be replaced by chlorine, while the new compound retains the basic type and characters. Aldehyde and chloral furnish an example of the same, in a body neither acid nor basic.

Here, then, is a fact of very general occurrence, which not only proves that the electro-chemical theory of combination is inapplicable, at all events in many cases, but also tends to establish a very different view : namely, that the electric character of an element is no permanent or essential property ; and that the type or character, or general properties of a compound, depend, not on the *nature*, but solely on the *arrangement* of its elementary atoms ; on the way in which they are grouped to form the compound molecule.

The reader will remember that, in the section on Isomorphism, the principle was laid down that the crystalline form of certain types of salts, such as the alum type, as well as many other properties of the compounds having those types, were the result of the *similar grouping* of *analogous elements*. We now see that, according to the law of substitution, as deduced from numerous careful observations, similarity of properties, or identity of type, are the result of similarity of grouping, even of elements not analogous, nay, of elements electrically opposed to each other. It is evident, therefore, that the arrangement of the elementary molecules to form the compound molecule is the circumstance on which depend almost exclusively the properties of the compound, or, in other words, the character of the type.

Substitution may be either complete or partial. In chloracetic acid, and in chloral, the substitution of chlorine for the hydrogen of the radical acetyle $C_4 H_3$ is complete. But when ether $(C_4 H_5) O$ is acted on by chlorine, the substitution takes place by successive steps, one equivalent of hydrogen being replaced at a time, after the oxygen has also been replaced by chlorine. Thus we have, first—

$$\begin{array}{ll}
\text{Ether or oxide of ethyle} & = (C_4 H_5)+O \\
\text{then, chloride of ethyle} & = (C_4 H_5)+Cl \\
\text{then, successively,} & C_4 \left\{\begin{matrix} H_4 \\ Cl^4 \end{matrix}\right. +Cl \\
 & C_4 \left\{\begin{matrix} H_3 \\ Cl_2^3 \end{matrix}\right. +Cl \\
 & C_4 \left\{\begin{matrix} H_2 \\ Cl_3^2 \end{matrix}\right. +Cl \\
 & C_4 \left\{\begin{matrix} H \\ Cl_4 \end{matrix}\right. +Cl \\
\text{and lastly,} & (C_4 Cl_5)+Cl
\end{array}$$

We thus obtain the series of compounds here indicated, in which the hydrogen is gradually replaced by chlorine, until at last we obtain the compound $(C_4 Cl_5)+Cl=C_4 Cl_6=2 C_2 Cl_3$, which is the perchloride of carbon. Most of these compounds have actually been obtained ; and it is obvious that they may all be referred to one type. Such a series is called a series of mechanical examples of the type in question, or rather of subtypes retaining the original character although modified.

In some cases, hydrogen has been replaced partly by chlorine, and partly by bromine. Laurent has described two compounds derived from naphthaline by substitution, the empirical formula for both of which is the following :—$C_{20} H_4 Cl_3 Br$. Yet the properties of these two compounds are quite distinct, and it is certain that this difference of properties must depend on a difference in the arrangement of the elements. Now, in the formation of these two compounds we have a very beautiful proof of the existence of a difference in the arrangement: for one is produced when chlorine acts on the compound called by Laurent bronaphtése, $C_{20} H_6 Br_2$; while the other is formed when bromine is made to act on chlonaphtise, $C_{20} H_5 Cl_3$. It is obvious that in the first case 2 eq. of hydrogen and 1 eq. of bromine are replaced by chlorine ; while in the second, 1 eq. of hydrogen is replaced by bromine. While, therefore, all four compounds may be deduced from the type $C_{20} H_8$, and while both the bromine and chlorine play the part of hydrogen, it is impossible to doubt that each of the 8 eq. of hydrogen has its special place in the compound molecule of the type, and that, in the two empirically identical formulæ above given, the 1 eq. of bromine does not replace the same eq. of hydrogen, and consequently the bromine occupies in the two compounds different positions. The same remark applies to the 3 eq. of chlorine.

We may illustrate our meaning as follows :—Let $C_{20} H_8$ be the type, and let each of the eqs. of hydrogen have a number attached indicating its place in the typical molecule. We shall then have

$$C_{20} \begin{Bmatrix} H_1 & H_2 & H_3 & H_4 \\ H_5 & H_6 & H_7 & H_8 \end{Bmatrix}$$

Now if we represent the two compounds above mentioned in the following manner, we can then conceive the influence of arrangement on the properties of two compounds having the same empirical formula. The first may be

$$C_{20} \begin{Bmatrix} H_1 & H_2 & H_3 & H_4 \\ Cl_5 & Cl_6 & Cl_7 & Br_8 \end{Bmatrix}$$

and the second may be

$$C_{20} \begin{Bmatrix} H_1 & H_2 & H_3 & Br_4 \\ Cl_5 & Cl_6 & Cl_7 & H_8 \end{Bmatrix}$$

It is only on this principle that we can explain the facts observed by Laurent; and it is easy to see that the above type, $C_{20}H_8$, will admit of innumerable modifications: for even the subtype $C_{20}H_4Cl_3Br$. is capable of yielding many more than the two above given; and the change of 1 eq. produces a new subtype, equally fertile in new forms.

In fact, Laurent has actually obtained, as will be shown further on, a very large number of what we have called subtypes from the type $C_{20}H_8$, which is naphthaline, and has established the same law in reference to many other types.

The preceding observations will, I trust, be found sufficient to convey a clear general notion of the prevalent doctrines of chemical types and of substitution, as applied to organic chemistry.

THE DECOMPOSITIONS AND METAMORPHOSES OF ORGANIC COMPOUNDS.

Organic compounds, whether actual organised tissues, unorganised products of animal and vegetable life, or new substances artificially produced, are generally characterised by a great proneness to undergo decomposition or metamorphosis. This instability is especially marked in those compounds which contain nitrogen, not only, because, containing four elements (in most cases), they are exposed to more numerous causes of change than such bodies as contain only three (carbon, hydrogen, and oxygen), but also because nitrogen is, in its relations to those three elements, the most remarkable element we know. According to the circumstances under which a change is induced, nitrogen may separate uncombined, as in the ultimate analysis of organic substances by combustion with oxide of copper or chromate of lead; or it may combine with oxygen, yielding nitric acid, as in nitrification; or with carbon, yielding the compound radical cyanogen, as when nitrogenised organic matter is ignited with carbonate of potash; or with hydrogen, yielding ammonia, as when nitrogenised organic matter is ignited with hydrated alkalies.

It is easy to see, therefore, that while all organic matter is prone to change, this is especially the case with nitrogenised compounds. In fact, many of these compounds cannot be kept more than a few hours without the commencement of decomposition or metamorphosis, in the shape of putrefaction or fermentation. This kind of metamorphosis will be separately considered hereafter: in the meantime it is important to observe, that when such a compound has entered into a state of decomposition, it acquires the properties of a ferment, that is, it is capable of inducing a similar metamorphosis in another compound, if placed in contact with it.

The true explanation of this fact appears to be, that the particles or molecules of the exciting body or ferment, being in a condition of change, and therefore in motion, communicate to the molecules of the body placed in contact with them an amount of motion sufficient to destroy the balance of the existing affinities; which in organic compounds is easily done, the chemical equilibrium being very unstable; and thus gives rise to a new play of affinities and the production of new compounds, as when sugar by contact with yeast is resolved into alcohol and carbonic acid.

But in addition to metamorphoses of the kind just alluded to, which, in the various ferments at least, commence spontaneously, air (at all events, at the commencement), moisture, and a certain temperature being the usual conditions, organic substances undergo very well marked decompositions when exposed to the action of heat and of some powerful re-agents; and it seems advisable here to give also a general account of such decompositions, as they admit of being classified under certain heads or rules generally applicable.

We shall here, therefore, briefly describe the changes produced on organic compounds: 1, by oxidation; 2, by the action of acids; 3, by the action of bases; 4, by the action of heat in close vessels, or the destructive distillation; and 5, by the contact of ferments.

1. *Oxidation: a. direct.*—The direct oxidation of organic compounds takes two distinct forms. The first is the familiar one of combustion, in which the action of the atmospheric oxygen is aided by a high temperature. The results differ according to the supply of oxygen. If there be an excess of air, or of oxygen, from any source, the whole of the carbon and

hydrogen is converted into carbonic acid and water, which, along with uncombined nitrogen, are the ultimate products of the action of oxygen on organic matters. But if the supply of air be deficient, the hydrogen is oxidised in preference to the carbon, which is deposited as smoke, soot, or lampblack.

The second form of direct oxidation is that which is commonly called decay, but which Liebig proposes to call Eremacausis (*i. e.* slow combustion), and which takes place when organic matter is exposed to air and moisture. In dry air it does not occur.

One of the most familiar examples of this kind of oxidation is that decay of wood by which it is slowly converted into a dark brown powder—ulmine. In this process, as De Saussure has shown, the wood absorbs oxygen, and produces an equal volume of carbonic acid along with water, and the residue—ulmine. As, in combustion, the oxygen combines by preference with hydrogen, so also in eremacausis there is every reason to believe that the absorbed oxygen combines with the hydrogen of the wood, and that an equivalent quantity of oxygen, also derived from the wood, is given off in the form of carbonic acid. Now, since wood may be represented as composed of carbon and the elements of water, and as water and carbonic acid are two of the products of eremacausis, it might be supposed that the water was ready formed in the wood, and that the absorbed oxygen had combined with the carbon. But it has been shown that, in presence of hydrogen, carbon does not at the ordinary temperature combine with oxygen, for which its affinity is less powerful; and besides, in the decay of wood, the proportion of carbon in the residue (the ulmine) is constantly greater than in the wood. Thus oak wood, $C_{36}H_{22}O_{22}$ yields in one stage of decay, ulmine, the composition of which agrees with the formula $C_{35}H_{20}O_{20}$; and in a more advanced stage, an ulmine of the formula $C_{34}H_{18}O_{18}$. Here we see that for every 2 eqs. of hydrogen oxidised by the air, 1 eq. of carbon and 2 eqs. of oxygen have been separated; so that the per centage of carbon in the residue constantly increases, and the final result of eremacausis would be a residue of carbon; were it not that, as the proportion of carbon in the ulmine increases, its affinity for the other elements, strengthened by its mass, becomes too powerful to be overcome by the oxygen of the air without the aid of heat.

Other examples of eremacausis are, the acetification of alcohol, and the process of nitrification in which ammonia undergoes eremacausis. These, as well as other instances, will be considered in their proper place.

Eremacausis is greatly promoted by heat and by the presence of alkalies. It is, on the contrary, arrested or retarded by cold, dryness, acids, and many salts, such as corrosive sublimate, which has been used to prevent the decay of wood.

There is one circumstance connected with eremacausis, or decay, as above described, which is worthy of special attention. It is, that a substance, in a state of eremacausis, if placed in contact with another, which is capable of undergoing this change, speedily causes the latter to enter into the same condition of change. This effect of contact may be compared, in one sense, to that of a body in combustion, which sets fire to other bodies; but in ordinary combustion the high temperature plays an important part, while in eremacausis the effect appears to be due to the communication of motion from the particles of the decaying body to those of the other substance, which motion, as in the case of fermentation, overturns the existing balance of affinities, unstable as it is in organic compounds, and gives rise to the formation of new products.

The process of eremacausis, or slow oxidation in the atmosphere, is one of very great practical importance, inasmuch as, by this means, the elements of dead organic matter are made to assume those forms—namely, the forms of carbonic acid, water, and ammonia—in which they are capable of contributing to the nutrition of new or growing vegetables.

A peculiar species of eremacausis is observed in the case of the simultaneous action of oxygen and ammonia on certain colourless vegetable products, which, absorbing these gases greedily, are thus converted into nitrogenised compounds of very fine blue or purple colours. Of this we have examples in orcine, erythrine, and phloridzine; and there is good reason to attribute the formation of indigo, from a juice devoid of blue colour, to an action of this kind, since both oxygen and ammonia appear to be necessary to its production. The transformation of alloxantine or of uramile into murexide also depends on the simultaneous action of ammonia and oxygen.

b. Indirect Oxidation. The indirect oxidation of organic compounds may be effected in a variety of ways, as, for example, by nitric acid, the action of which we shall presently describe along with that of other acids; by certain salts, as by permanganate of potash, which converts sugar, for example, into oxalic acid; or by the employment of a mixture of bichromate of potash and diluted sulphuric acid, by which means salicine may be made to yield the hyduret of salicyle (oil of spiræa); or, finally, by the combined action of heat and hydrated alkalies, as when indigo, heated with potash, gives rise to anthranilic acid, hydrogen being given off; or acetates, heated with baryta, yield marsh gas and carbonates.

2. *Action of Acids on Organic Compounds.* This action is very various; the two acids most frequently employed are the nitric and sulphuric acids, and, as might be expected, the former acts more as an oxidising agent than the latter.

When sugar, for example, is heated with nitric acid, the latter loses oxygen, for nitrous acid is given off in enormous quantity; while the elements of the sugar, by the action of the oxygen are made to combine so as to produce compounds of less complex radicals than that of sugar probably is. Among the products are water, carbonic acid, oxalic acid, and saccharic acid, besides others not yet investigated; but the three first sufficiently show the tendency of oxidation to promote the formation of less complex radicals.

When nitric acid acts on organic matters, there is generally found one acid, if not more, among the products, and in this way a large number of acids have been discovered. Examples of this are, mucic acid from gum; indigotic and carbazotic acids from indigo; margaric acid from stearic acid; suberic and succinic acids from oily acids, besides many others. It frequently happens that compounds, whether acid or neutral, formed by the action of nitric acid on organic matter, contain hyponitrous acid as a constituent, apparently substituted for some element. This is the case with nitrobenzide from benzine, and with nitronaphthalase, and a whole series of compounds discovered by Laurent in his study of the action of nitric acid on naphthaline. The carbazotic or nitropicric acid also appears to contain a compound of nitrogen and oxygen. Some organic bases, as morphia and brucia, strike a deep red colour with nitric acid.

When sulphuric acid is made to act on organic compounds, it chars a considerable proportion of them by virtue of its attraction for oxygen and hydrogen in the form of water. But in many cases it produces very different effects. Thus, by boiling with sulphuric acid and water, starch and lignine are converted into grape sugar. In other cases, the sulphuric acid seems to lose so much oxygen as to produce hyposulphuric acid, which enters into combination with an organic compound, forming a new acid, as when sulphuric acid acts on naphthaline, and forms sulphonaphthalic acid; or on benzoic acid, forming hyposulphobenzoic acid; or on alcohol under certain circumstances, when an acid is produced containing the elements of hyposulphuric acid and of a carbo-hydrogen. In other cases, the sulphuric acid combines unchanged with the organic compound, as in sulphovinic acid, which is a bisulphate of oxide of ethyle ; sulphomethylic acid, and others.

Many organic compounds, heated with excess of sulphuric acid, are entirely decomposed, yielding water which combines with the acid, and other products which are disengaged. Thus oxalic acid is resolved into water, carbonic acid, and carbonic oxide ; formic acid into water and carbonic oxide ; alcohol into water, olefiant gas, and other products.

Several organic compounds are dissolved by sulphuric acid with the production of a fine red or purple colour. Salicine strikes a red colour with the acid, and cedriret, one of the constituents of tar, dissolves in it with a deep blue colour, as does also naphthalase.

Phosphoric acid may be employed in some cases to remove water from organic compounds, as it does not char them. Like sulphuric acid, it forms with oxide of ethyle an acid salt, known as phosphovinic acid.

Hydrochloric acid and its congeners have no very extensive action on organic substances. With alcohol, hydrochloric acid gas yields chloride of ethyle ; and a current of this gas, passed through an alcoholic solution of a fatty acid, gives rise to the compound of the fatty acid with oxide of ethyle, which would otherwise be obtained with difficulty. With oil of turpentine, oil of lemons, and some other essential oils composed of carbon and hydrogen, hydrochloric acid gas combines, forming solids resembling camphor. Pyroxanthine, a substance contained in tar, dissolves in strong hydrochloric acid with a fine and deep purple colour.

3. *Action of Bases on Organic Compounds.* Hydrated bases unite, of course, with organic acids ; and when heated with neutral substances, they generally give rise to the formation of acids, such as acetic and oxalic acids, or even carbonic acid, oxygen being taken from the water of the base, and hydrogen being disengaged, or, (if the organic body contain nitrogen,) hydrogen and ammonia. This property of hydrated bases is employed as a means of converting all the nitrogen of organic compounds into ammonia, and in this form determining its quantity.

The presence of bases greatly promotes the absorption of atmospheric oxygen by organic substances. This is the reason why alkalies assist eremacausis. The same effect is very conspicuous in the change which the salts of gallic acid (and some other acids) undergo when exposed to the air. A solution of an alkaline gallate absorbs oxygen very rapidly, and becomes very dark in colour, being oxidised in a far shorter time than if the acid had been uncombined.

4. *Action of Heat on organic Compounds in close Vessels.* This action is known under the name of the *destructive distillation.* It must be considered as a combustion with a very limited supply of oxygen, that namely afforded by the substance itself. A very great variety of compounds is produced, many of them very interesting and useful. The destructive distillation may be considered as it affects substances containing nitrogen, and substances devoid of that element. Many products are common to both cases, but many also are confined to one case, especially to that of nitrogenised substances.

The destructive distillation of non-nitrogenised substances has been chiefly studied in the case of wood, which, when heated in close vessels, yields a great variety of products: some, binary compounds, such as paraffine, naphthaline, eupione, water, carbonic oxide, carbonic acid, marsh gas, and olefiant gas: others ternary, such as acetic acid, $C_4H_3O_3$; hydrated oxide of methyle or pyroxylic spirit, $(C_2H_3)O,HO$; lignone, xylite, mesite, and other volatile etherial liquids, composed of the same elements as pyroxylic spirit, and very similar to it in properties; creosote; picamar; capnomore; cedriret; pittacal, and pyroxanthine, besides many others, not yet properly investigated.

When fatty or resinous bodies are subjected to the destructive distillation, there are obtained, besides other compounds, two solid carbo-hydrogens: chrysene, C_3H, and pyrene, $C_{10}H_2$; which also occur among the products of the distillation of coal.

This latter distillation may serve as an example, the best known, of the action of heat on nitrogenised organic bodies; for coal contains a certain although small proportion of nitrogen. The products, besides creosote, paraffine, naphthaline, and probably several others of those obtained from wood, include much ammonia, hydrocyanic acid: some peculiar non-nitrogenised acids, as carbolic acid, $C_{12}H_5O,HO$, (a remarkable compound, having an odour resembling that of creosote, and yielding, when subjected to various re-agents, an extensive series of new compounds [Runge, Laurent];) rosolic and brunolic acids; and two very remarkable nitrogenised bases, containing no oxygen, namely, kyanol (*aniline, crystalline,*) $C_{12}H_7N$, and leukol, $C_{18}H_8N$; besides a third, not yet fully investigated, pyrrol; finally, paranaphthaline, or anthracene, $C_{30}H_{12}$, and coal tar naphtha, which is used as a solvent for caoutchouc.

The distillation of animal matter, such as hoofs, horns, or bones, yields analogous results, but is characterised by the very large amount of ammonia which is obtained, animal matter being richer in nitrogen than coal is. This ammonia appears as carbonate, which salt is thus manufactured, and hence was and occasionally still is, called salt of hartshorn.

Many organic acids, when heated in close vessels to a certain temperature, short of the destructive distillation, undergo a remarkable decomposition; carbonic acid is given off, and there remains a new acid, which is called a pyrogenous acid, or pyro-acid. Thus meconic acid, at a certain temperature, yields carbonic acid and komenic acid: while komenic acid, if heated in its turn, yields carbonic acid and pyromeconic acid. We have also pyromucic, pyrotartaric, or pyroracemic and pyrocitric acids; citric acid yielding three pyro-acids, aconitic, (equisetic), itaconic and citraconic acids, and malic acid also yielding two, maleic and paramaleic or fumaric acids.

From the above statements, it is obvious, that the action of heat on organic compounds gives rise to a very large number of important products, of which only the most remarkable have been named. All will be described in their proper places.

5. *Action of ferments on organic compounds.* Of this action the best known and most important example is the fermentation of sugar, by which it is resolved into alcohol and carbonic acid.

The circumstances under which this metamorphosis occurs are these: the sugar must be dissolved, the solution must have a certain temperature, and there must be present a ferment, such as yeast or some analogous body. In the juice of the grape a ferment, the fibrinous or caseous constituent of the juice is naturally present; and Gay Lussac showed that the contact of atmospherical air was necessary to commence the fermentation, but that this contact with the atmosphere might be only for a very brief period, after which air was no longer necessary. It is obvious that the air acts by inducing a state of change in the ferment, for if any ferment, previously exposed to the air, be added to a pure solution of sugar, fermentation will take place without the mixture being exposed to the air after the ferment has been added.

Berzelius and others conceive that the ferment acts by contact in some way not very clearly defined, by catalysis, as it is called, as they conceive sulphuric acid to do in the formation of ether from alcohol. But Liebig has proved that in this latter case the acid first combines with ether (oxide of ethyle) forming sulphovinic acid (bisulphate of oxide of ethyle), and that this compound at a temperature rather higher than that at which it is formed, is decomposed into hydrated sulphuric acid and ether which distils over. The same chemist has pointed out many other instances of the effect of contact, even in inorganic chemistry: such as the action of oxide of silver on peroxide of hydrogen, where the former compound, by contact with the latter, not only decomposes it, causing oxygen to be rapidly given off, but is itself decomposed, losing all its oxygen; the solution in nitric acid of an alloy of platinum and silver, while platinum alone is insoluble in that acid; or the action of carbonate of silver on certain organic acids, which cause a disengagement of carbonic acid, this disengagement being attended with a partial reduction of the oxide of silver.

These, and many other, more familiar cases, particularly those where a compound is decomposed with detonation in consequence of a slight touch, or gentle friction, a moderate elevation of temperature, or the contact of another substance (*e. g.* chloride of nitrogen with oil) all tend, according to Liebig, to establish the doctrine that in certain compounds the balance of affinities is unstable, and therefore easily overturned, either by chemical or by mechanical influences.

The compounds which are capable of fermentation or any similar metamorphosis, are all of them bodies in which such an unstable equilibrium exists: they are all, in point of fact, easily decomposed by many different agencies, such as heat, acids, bases, oxygen, chlorine, &c. &c. Now, we can offer no other explanation of these facts of fermentation than this, that when a body in a state of progressive change, the particles of which are consequently in a state of motion, is placed in contact with another body, the particles of which are in a state of unstable equilibrium, the amount of motion mechanically communicated to the particles of the latter from those of the former, is sufficient to overturn the existing equilibrium, and by the formation of a new compound establish a new equilibrium more stable under the given circumstances.

There is nothing unphilosophical in this explanation, and it is to be considered as the best theory of fermentation yet attempted. According to the view of Liebig, a ferment is merely a compound in a state of decomposition, capable of setting in motion, and thereby bringing also into a state of decomposition, the particles of another compound, the existence of which depends on a nice balance of affinities.

On the other hand the view adopted by Berzelius, according to which fermentation, and all the other phenomena of chemical change produced by contact are the results of a peculiar unknown force, the catalytic force, coming into action when certain bodies are placed in contact, appears unphilosophical, as, in the first place, assuming the existence of a new force where known forces would suffice to explain the facts; and, secondly, as furnishing no real explanation, but merely acknowledging, indirectly, our inability to offer any such explanation. When we ascribe an effect to catalysis, we are only saying, in other words, that we cannot account for it; catalysis is thus merely a convenient term for all that we do not understand. And to the use of the word in this sense, namely, as a name for the agent which produces certain effects, the agent itself being unknown, there would be no objection, were it not that catalysis has been employed to account for phenomena not only different from each other, but actually of an opposite kind. For example, platinum, in causing *the combination* of oxygen and hydrogen, is said to act catalytically, and the action of oxide of manganese, or oxide of silver in decomposing peroxide of hydrogen, that is, in causing *the separation of* oxygen and hydrogen, is also called catalytic. This example proves how loosely the word has been employed, and how vague are the views which have led to its introduction.

A variety of important and interesting processes come under the head of actions caused by ferments; the production of alcohol from sugar, of oil of bitter almonds from amygdaline, and of lactic acid from sugar of milk, are all examples of this; and in each of these cases, the ferment is peculiar. In the case of sugar it is yeast, or gluten undergoing eremacausis and putrefaction; in the case of amygdaline it is emulsine, a peculiar modification of albumen; and in the case of sugar of milk it is caseine, the nitrogenised constituent of the milk.

The access of air is required at first to yield oxygen to the gluten, &c., which then entering into eremacausis, or if air be excluded, into putrefaction, are capable of acting as ferments.

In the actions induced by ferments, we are to distinguish those in which some external element or elements are added to those of the compound, which cases resemble ordinary decompositions, from those in which the elements of the decomposed body merely transpose themselves, producing new compounds. The latter are properly and strictly termed metamorphoses. Fermentations, in which oxygen is absorbed, are examples of eremacausis, and it has already been mentioned that a body in a state of eremacausis acts on other bodies as an excitant of the same change, that is, as a ferment.

Indeed, most ferments, whether they induce eremacausis, or a more pure metamorphosis in other bodies, are themselves in a state of eremacausis, at all events in the commencement of the change.

The subject of fermentation and ferments will be hereafter more especially considered, in connexion with fermentescible compounds: here the subject is merely treated in a general way.

Putrefaction, under ordinary circumstances, partakes largely of eremacausis, and differs from the ordinary kind only in the offensive odour of some of the products, chiefly compounds of sulphur and phosphorus, as sulphuretted and phosphuretted hydrogen. When air is excluded, putrefaction goes on, provided moisture be present, and it is then a metamorphosis, giving rise, in the case of vegetable matter putrefying under water, or in the strata of mines, to gaseous products, such as marsh gas and olefiant gas, constituting with air the fire-damp, and carbonic acid, which is the choke-damp, of the miner.

Animal matter, in a state of putrefaction, as putrid flesh, blood, cheese, or wine, acts as a ferment, and is capable of causing the metamorphosis of sugar into alcohol and carbonic acid, as well as of inducing eremacausis, and also propagating a putrefactive decomposition analogous to its own. Thus, it is well-known that fresh cheese, if inoculated with decaying cheese, soon passes into decay, spreading from the seat of the inoculation.

We shall, hereafter, see that it is probable that some poisons and miasmata act as ferments on the blood. The singular sausage poison of Wurtemburg is animal matter in a peculiar state of decay, and does not contain any poisonous *compound*, only a poisonous *state* or *condition;* and the same principle may hereafter be found to furnish the true explanation of contagions.

Fermentation, putrefaction, and eremacausis are all promoted by the same circumstances, and arrested by the same influences. Antiseptics are substances which by combining with the ferment, or a part of it, or even with the body to be fermented, prevent the continuance either of the decomposition in the ferment, or of the fermentation itself. Corrosive sublimate and arsenic, which are powerful antiseptics, combine with animal matter, and form with it stable compounds; creosote combines energetically with albumen, &c., &c.

In fermentation, properly so called, the elements of the ferment take no chemical share in the metamorphosis of the body acted on by the mechanical agency above explained. That body is resolved into two or more new compounds of less complex radicals. The elements of water may or may not take part in the change; when they do, as in the case of sugar, the weight of the products, in this case alcohol and carbonic acid, is equal to that of the sugar, *plus* a certain weight of water. As, when the water is passed in vapour over carbon at a white heat, the carbon is shared between the oxygen and hydrogen, producing carbonic acid (or oxide), and carburetted hydrogen, so in the metamorphosis of sugar, and other analogous cases, we have on the one hand an oxidised compound, (in the case of sugar represented by carbonic acid), and on the other a compound in which part of the carbon is united to all the hydrogen (in the case of sugar, the alcohol). Similar results are obtained when alcohol or acetic acid are metamorphosed by heat, and this may be viewed as a general character of the metamorphosis of non-nitrogenised bodies: namely, that the carbon is divided between the oxygen and hydrogen.

In putrefaction, again, the ferment plays a chemical part in the change, and two or more compounds, the ferment and the putrefying body or bodies, combine to give rise to new compounds, with or without the elements of water. Putrefaction is generally the characteristic transformation of nitrogenised compounds, and the very great tendency of such compounds to undergo transformations is well illustrated by the spontaneous metamorphosis of a solution of cyanogen in water. Such a solution contains the four principal elements of organic bodies; and its transformations may be said to be the only case of putrefaction which has been as yet carefully studied.

The solution after a time becomes brown and turbid, and deposits a dark matter, containing ammonia, united to a compound formed of the elements of cyanogen along with those of water. This matter being insoluble, undergoes no further change. Such a compound might arise from the reaction between 2 eq. cyanogen, and 4 eq. water: thus, $2\,C_2N+4\,HO=NH_3+(C_4HNO_4)$; according to some, the brown matter contains no ammonia, and is $C_4N_2HO=2\,C_2N+HO$.

Another change is that in which water is decomposed, each of its elements uniting with cyanogen, and producing cyanic and hydrocyanic acids; thus: $2\,HO+2\,C_2N=(C_2N,\ O+HO)+H,\ C_2N$.

Another metamorphosis gives rise to oxalic acid and ammonia. In this case, 1 eq. cyanogen acts on 3 eq. water; thus: $C_2N+3\,HO=NH_3+C_2O_3$.

But cyanic acid cannot exist in contact with water and other acids: it is instantly metamorphosed into bicarbonate of ammonia; thus: $C_2NO+3\,HO=NH_3+2\,CO_2$.

Towards the end of the process, when ammonia has become predominant, the cyanic acid produced undergoes a different metamorphosis. It now unites with water and ammonia, and may possibly for a time exist as hydrated cyanate of ammonia: but at all events that salt, if formed at all, is soon transformed into urea. $NH_3+C_2NO+HO=C_2H_4N_2O_2=$urea.

Again, the hydrocyanic acid gives rise to another brown solid body containing cyanogen or paracyanogen (possibly mellone also), and hydrogen ; and, along with this, oxalic acid, urea, and carbonic acid, by metamorphoses already described.

Lastly the hydrocyanic acid in contact with water, and an acid or an alkali (here oxalic acid or ammonia), undergoes another metamorphosis, and is transformed into formic acid and ammonia ; thus : $H, C_2 N + 4 HO = NH_3 + C_2 HO_3, HO$.

Thus cyanogen, a binary compound, along with water, another binary compound, gives rise to no less than eight different compounds ; 1st, the black compound, containing the elements of cyanogen and those of water, possibly $C_4 H N_2 O$: 2nd, ammonia, NH_3 : 3rd, cyanic acid, $HO, C_2 NO$. 4th, hydrocyanic acid, $H, C_2 N$. 5th, oxalic acid, $C_2 O_3$: 6th, carbonic acid : 7th, a brown solid, containing cyanogen (paracyanogen) and hydrogen : 8th, formic acid, $C_2 HO_3, HO$: and in addition to these, three bodies, formed by the combination of two of the above eight, and containing all the four elements ; namely, 9th, oxalate of ammonia : 10th, bicarbonate of ammonia : 11th, urea.

This striking example is well adapted to give a clear idea of the immense variety attainable, when, instead of two binary compounds, two ternary or two quaternary compounds, along with water, are concerned ; and of the slight modifications of external circumstances which are required to produce results so varied, all the above substances being produced in a liquid at the usual temperature.

It is hoped that the above sketch of the doctrine of the chemical changes and metamorphoses of organic compounds will suffice to enable the student to follow the individual processes and reactions, to be hereafter mentioned, which, owing to our limited space, we must treat with great brevity. We shall now conclude our introductory matter by some general observations on the doctrines now held by many chemists on the subject of the organic acids ; after which we shall enter on the study of the known organic radicals.

ORGANIC ACIDS.

The acids met with in organic chemistry are principally compounds of carbon, hydrogen, and oxygen, although some do contain also nitrogen. They are distinguished from inorganic acids by their high atomic weight, and by the action of heat, which decomposes them all. As, in many of them, the oxygen they contain is a multiple by a whole number of the oxygen of the bases which neutralise them, so they are viewed as oxygen acids by those who consider true sulphuric acid to be an oxygen acid, SO_3, and oil of vitriol to be its hydrate,

HO, SO_3. In the case of acetic acid, for example, the formula of which is $(C_4 H_3) O_3 HO$, the compound $(C_4 H_3) O_3$, unknown in a separate form, is called dry acetic acid, and the strong acetic acid is considered as its hydrate; and the analogy is supposed to be fortified by the fact that dry acetic acid, like dry sulphuric acid, contains 3 eq. oxygen, and neutralises 1 eq. of base, MO, containing 1 eq. of oxygen.

But a careful study of the organic acids leads us to apply to them the same theory which we have already adopted for the inorganic acids, and to consider them as compounds of hydrogen, with compound radicals, usually consisting of carbon, hydrogen, and oxygen. On this view, as oil of vitriol is H, SO_4, the strongest acetic acid is $H, (C_4 H_3) O_4$. It is true that this radical, $(C_4 H_3) O_4$, does not exist, or is not known in the separate form; but the same remark applies to dry acetic acid, $(C_4 H_3) O_3$, which on the old view is supposed to be combined with water, for it also is unknown in the separate state.

The existence of compound radicals in organic acids is not more difficult to imagine than that of SO_4 the compound radical of sulphuric acid, for $(C_4 H_3) O_4$ only differs from it in containing three elements instead of two; indeed, as some ternary organic radicals are known in the separate form, we actually derive an argument from organic acids in favour of the existence of compound radicals in inorganic acids. Thus, the radical or organic metal, kakodyle, forms kakodylic acid.

But we find, among organic acids, a much larger proportion which are bibasic, tribasic, in short polybasic, than occurs among inorganic acids. Referring to what was said of the monobasic, bibasic, and tribasic phosphoric acids, it will be easily understood that while acetic acid, for example, is monobasic, tartaric acid, malic acid, komenic acid, alloxanic acid, and others are bibasic; that citric acid and mekonic acid are tribasic, and that saccharic acid is quinquebasic. And as the three modifications of phosphoric acid were described on the old view as monohydrated, bihydrated, and terhydrated, and on the new view, as containing, respectively, 1, 2, and 3 eqs. of hydrogen, replaceable by metals, so tartaric acid may be either $C_8 H_4 O_5, 2 HO$ or $C_8 H_4 O_7, H_2$; malic acid may be $C_8 H_4 O_8, 2 HO$ or $C_8 H_4 O_{10}, H_2$; and so on; while citric acid may be either $C_{12} H_5 O_{11}, 3 HO$ or $C_{12} H_5 O_{14}, H_3$, and meconic acid, $C_{14} HO_{11}, 3 HO$, or $C_{14} HO_{14}, H_3$; and lastly, saccharic acid may be $C_{12} H_5 O_{11}, 5 HO$; or $C_{12} H_5 O_{16}, H_5$.

In such polybasic acids, there is always some hydrogen in the radical, of which it is a constituent, and some combined with the radical, and replaceable by its equivalent of metals. It is only this latter hydrogen, the amount of which affects the neutralising power of the acid.

Now, among the phenomena of the action of bases on organic acids, we have some facts which seem almost to demonstrate the existence of this replaceable hydrogen, as such, and thus to establish the new theory of acids. Thus, meconic acid, which is tribasic, forms, like tribasic phosphoric acid, three series of salts, in which 1, 2, or 3 eqs. of hydrogen are replaced by metal. But while the meconic acid, as well as the tribasic phosphoric acid, readily forms with oxide of the silver, the salt in which all the hydrogen is replaced by silver ; it cannot form, or forms with difficulty, a similar salt with potash, with which it forms very easily salts with 1 and 2 eqs. of metal, and 2 or 1 eqs. of hydrogen. Here we have the apparent contradiction of a weak base, oxide of silver, neutralising the acid easily and completely ; while a strong base, potash, leaves it imperfectly neutralised. This cannot, I think, be accounted for on the old view, and many similar cases might be mentioned. On the new view, such apparent anomalies disappear : for since the neutralising depends on the replacement of hydrogen by a metal, it is evident that an oxide which is easily reduced, or deprived of its oxygen by hydrogen, like oxide of silver, will most easily neutralise acid, while a difficultly reducible oxide, such as potash, cannot be so far reduced as to yield 3 eqs. of metal, so as to form the neutral salt.

There are other kinds of organic acids which are what may be called coupled acids ; that is to say they contain an acid coupled with another body, which does not neutralise the acid, but accompanies it in all its combinations. Thus, in hyposulphonaphthalic acid, $C_{20}\ H_8\ S_2\ O_5$, HO, we have hyposulphuric acid $S_2\ O_5$, coupled with naphthaline, $C_{20}\ H_8$, and the coupled acid neutralises exactly as much base as the hyposulphuric acid alone would do. Again, formobenzoilic acid $C_{16}\ H_7\ O_5$, HO, may be viewed as a coupled acid, consisting of formic acid $C_2\ HO_3$, HO and oil of bitter almonds (hyduret of benzoyle) $C_{14}\ H_6\ O_2$, which neutralises just as much base as the formic acid alone. Those coupled acids which contain hyposulphuric acid, as is often the case, are formed by the action of oil of vitriol, or of anhydrous sulphuric acid, on organic bodies, when 2 eqs. of acid, losing 1 eq. oxygen, form hyposulphuric acid ; which commonly unites with the organic matter *minus* 1 eq. hydrogen, that hydrogen having combined with the oxygen derived from the sulphuric acid.

In the following pages we shall adopt the arrangement of Liebig, which has the advantage of uniting those substances which are naturally allied in composition. It proceeds, in the first place, on the principle of describing, under each known or admitted organic radical, all the compounds derived from or closely connected with it. After having gone through these, it takes up the consideration of the best known organic acids, including the oily acids; then the neutral oils, fat and essential; the resins; the non-nitrogenous colouring matters, bitter and extractive principles, nitrogenised colouring matters and their congeners; the organic bases; starch; gum; woody fibre; destructive distillation of wood, of lignite, of coal; nitrogenised and sulphurised vegetable principles, albumen, &c. the modifications of these in the animal kingdom: bile: nervous matter: gastric juice: saliva: excrements: urine: blood: lymph, &c. And the whole is wound up with considerations on the nutrition of plants and animals.

This arrangement is not a scientific one, and in the present state of our knowledge such an arrangement is, I fear, unattainable. But it is very convenient, and, by judicious grouping, very much facilitates the learning and the retaining in the memory of the immense mass of facts which at present constitute organic chemistry.

We proceed, therefore, to consider those organic radicals which are admitted by the best authorities, although they are not always known in the separate state. The first compound radicals that attract our attention are certain binary ones, already mentioned as binary compounds, but not in their character of radicals, in the first Part of this work; these are amide or amidogen, cyanogen, and carbonic oxide.

I. Amide. $NH_2 = Ad = 16{\cdot}19$.

Syn. *Amidogen*.—It has already been mentioned that certain compounds exist, in which we can hardly doubt that this substance is present. Thus, potassium or sodium, heated in dry ammoniacal gas, disengages 1 eq. of hydrogen, forming the compound KNH_2 or $NaNH_2$. When these are put into water, potash or soda is formed, while ammonia is set free: $K, NH_2 + HO = KO + NH_3$. Again, when oxalate of ammonia, NH_3, HO, C_2O_3 is heated, there are formed, water which distils over, and the compound $NH_2C_2O_2$ which remains behind: thus, $NH_3, HO, C_2O_3 = 2HO + NH_2C_2O_2$. The latter compound is called oxamide, and is a sparingly soluble white powder, neutral or indifferent in itself, but yielding, when digested with an alkali, ammonia, which escapes, and oxalic acid, which combines with the alkali. Or if oxamide be heated with diluted sulphuric acid, it yields ammonia which combines with the acid, and oxalic acid which crystallises in cooling. In both cases water is decomposed: thus $NH_2C_2O_2 + 2HO = NH_3, HO + C_2O_3$.

Now oxamide is interesting, as being the type of a class of compounds, all of which, when heated with an alkali or an acid, yield ammonia and an acid, the ammonia and the anhydrous acid together containing just 1 eq. of water more than the compound which, with the aid of water, has yielded them. If we consider oxamide as $NH_2 + C_2O_2$; that is, as composed of amide (or ammonia *minus* hydrogen NH_2), and the radical carbonic oxide (or oxalic acid *minus* oxygen C_2O_2), then all its congeners are likewise compounds of amide, on the one hand, and an anhydrous organic acid, *minus* oxygen, on the other. On this view benzamide is benzoate of ammonia, *minus* water, $(NH_3 + C_{14}H_5O_3, HO) - 2HO = NH_2 + C_{14}H_5O_2$; or it is amide *plus* benzoyle (the radical of benzoic acid, $C_{14}H_5O_2$). Therefore, when benzamide is acted on by potash, ammonia is given off, and benzoate of potash is left; and when it is heated with an acid, a salt of that acid with ammonia is obtained, while benzoic acid crystallises. There are a good many similar compounds which are called amides, and are viewed as compounds of amide.

It is obvious that the distinctive characters of amide, which is not known in the separate form, are its powerful affinity for hydrogen, and its equally strong tendency to combine with radicals which have a very great affinity for oxygen, such as those already mentioned, potassium, sodium, the radical C_2O_2, and the radical benzoyle.

With hydrogen amide forms two compounds, ammonia, Ad H, and ammonium, AdH_2. The former may be called, in this view, hydramide. The latter, as has been already explained (at p. 67), is considered to be a compound metal.

It is very remarkable, that when ammonia or hydramide combines with an acid, the resulting compound is not a salt, unless the acid contain hydrogen. Thus, hydramide, with dry sulphuric acid, SO_3, forms a compound which is not sulphate of ammonia, and is not a salt at all. But if, instead of SO_3, we employ oil of vitriol, HO, SO_3, or H, SO_4, sulphate of ammonia, a true salt, is obtained.

Here we may conclude that Ad H, in contact with H, SO_4, takes the hydrogen, forming ammonium, and that the resulting salt is composed of $AdH_2 + SO_4$; that is, a metal combined with the sulphuric acid radical, just as sulphate of potash is

K, SO_4. In all the true salts of ammonia, therefore, $Ad\,H_2 = Am$ (Ammonium) occupies the place of a metal, and may be replaced by a metal ; and even if we consider sulphate of potash to be KO, SO_3, we have only to view the sulphate of ammonia as $NH_4\,O, SO_3 = Ad\,H_2\,O, SO_3 = Am\,O, SO_3$, that is, sulphate of oxide of ammonium.

It must be borne in mind, however, that although all the chemical relations of these compounds confirm the ammonium theory, yet neither ammonium nor its oxide are capable of existing uncombined ; for ammonium, when separated, is resolved into ammonia and hydrogen ; and oxide of ammonium, when separated, assumes the forms of ammonia and water.

Of the chief compounds of amide, ammonia or hydramide has been previously described. It remains for us to direct attention to this substance as constantly present in the atmosphere in minute quantity, from whence it descends in the rain, being an absolutely indispensable agent in vegetation. We have already seen that the putrefaction and eremacausis of nitrogenised compounds yields carbonate of ammonia as a product. Its presence in the air is therefore certain, *à priori,* even although we cannot detect it until it is condensed and accumulated in rain. It is, however, absorbed from the air by almost all minerals and soils, especially aluminous and ferruginous soils ; hence a trace of ammonia is often found where it is not looked for, and where it has been erroneously believed to have been formed by the direct union of hydrogen and nitrogen. This is the true explanation of the very remarkable and accurate experiments of Faraday, which have lately been confirmed by Will and Varrentrapp.

As an ingredient of manures, ammonia is most valuable. Its action on growing vegetables will be hereafter explained.

Ammonia forms a large number of compounds with the oxides of metals, the chlorides of metals, of sulphur and of phosphorus, and finally with salts in general. These belong rather to inorganic chemistry, and the limited size of this work forbids us to describe them in detail.

But it is proper here briefly to notice the compounds formed by amide with metals, inasmuch as amide is here viewed as an organic radical, and some of these compounds are very important in reference to organic chemistry.

Amide then forms compounds with potassium, sodium, mercury, copper, silver, and platinum. The two former are of a greenish olive colour, and their action on water has been described above. The amide or amidide of mercury, $Hg\,Ad$, is not known in a separate state, but forms with bichloride of mercury the salt called white precipitate, $Hg\,Ad + Hg\,Cl_2$.

This salt is prepared by adding ammonia to a solution of bichloride of mercury. When boiled with potash, it yields another salt, $Hg\,Ad + Hg\,Cl_2 + Hg\,O_2$. The amidide of mercury also combines with the basic sulphate, and the basic nitrates of the same metal, forming, with the basic protonitrate, the soluble mercury of Hahnemann.

The amidide of copper, Ad Cu, is only known in combination with the hyposulphate and with the nitrate of ammonia.

The amidide of silver, Ag Ad, is known in combination with the nitrate, sulphate, seleniate and chromate of ammonia.

But it is the amidide of platinum which offers the greatest interest, as it gives rise to several very singular compounds, exhibiting the characters of very powerful bases. These remarkable substances have been studied by Gros, Reiset, and very recently by Peyrone, but are yet far from being understood. We shall endeavour briefly to state what is known of them.

When bichloride of platinum, $Pt\,Cl_2$, is heated for some time to nearly the melting point of tin, it loses half its chlorine, and is converted into protochloride, Pt Cl, which forms a powder of a dirty brownish green colour, insoluble in water. By continued digestion in ammonia, with the aid of heat, the protochloride is first changed into a green crystalline compound, which finally dissolves entirely, forming a yellowish solution, which on evaporation deposits yellowish white prismatic crystals. The green crystalline compound, discovered by Magnus, contains the elements of protochloride of platinum and those of ammonia, $Pt\,Cl\,N\,H_3$; the yellowish white crystals, discovered by Reiset, contain twice as much ammonia and the elements of water, $Pt\,Cl, 2\,N\,H_3 + aq.$

These two compounds are very remarkable; neither of them contains ammonia as such; both are insoluble in hydrochloric and dilute sulphuric acids. But the green compound of Magnus dissolves in nitric acid, with evolution of nitrous acid, and the solution on cooling deposits white crystalline scales, while the liquid contains no ammonia. These white scales, discovered by Gros, are the nitrate of a new base, $Pt\,Cl\,N_2H_6O$; which may be derived from 2 eq. of the insoluble compound of Magnus, $Pt_2Cl_2N_2H_6$, by the loss of 1 eq. of protrochloride of platinum and the addition of 1 eq. of oxygen. This base acts exactly like the basic oxide of a metal, or like oxide of ammonium, $N\,H_4O$, combining with acids and forming neutral salts. It not only forms salts with nitric and sulphuric acids and the like, but with hydrochloric acid it yields a heavy crystalline powder, which is a chloride, bearing the same relation to the base as chloride of ammonium, $N\,H_4Cl$ (sal ammoniac) does to oxide of ammonium.

This chloride, therefore, is $Pt\,Cl\,N_2H_6Cl$, and the radical of the oxide or base and of the chloride, will be $Pt\,Cl\,N_2H_6$, corresponding to ammonium, $N\,H_4$. Although Gros did not isolate either the radical or its oxide, yet from the characters and composition of its salts, there can be no doubt of its existence. If we represent this radical, $Pt\,Cl\,N_2H_6$ by R, then we have

$R\,O$ = oxide, the base of the salts, analogous to $K\,O$ or $N\,H_4$, O.
$R\,O + S\,O_3 = R + S\,O_4$ = sulphate, analogous to $K, S\,O_4$
$R\,O + N\,O_5 = R + N\,O_6$ = nitrate, analogous to $K, N\,O_6$
$R\,Cl$ = chloride, analogous to $K\,Cl$ or $N\,H_4, Cl$

The soluble crystalline compound of Reiset, $Pt\,Cl\,N_2H_6 + aq.$ when heated to 212°, becomes anhydrous, and is then $Pt\,Cl\,N_2H_6$, that is, it has the same composition as the radical of the base and salts of Gros. But it is not this radical; on the contrary, it is the chloride of a different radical, $Pt\,N_2H_6$, and its true formula is $Pt\,N_2H_6 + Cl$.

This new radical is also perfectly analogous to ammonium, as may be exhibited in a tabular form as follows.

	Chlorine Compound.	Sulphate.	Nitrate.	Double Chloride with Platinum.
Ammonium $N\,H_4 = Am$	$Am\,Cl$	$Am\,S\,O_4$	$Am\,N\,O_6$	$AmCl + PtCl_2$
Radical of Reiset $\}\ PtN_2H_6 = R'$	$R'Cl$	$R'\,S\,O_4$	$R'\,N\,O_6$	$R'Cl\ + PtCl_2$

In the case of ammonium, we cannot isolate the oxide $Am\,O = N\,H_4O$, as it instantly resolves itself into ammonia and water, $N\,H_3 + H\,O$. But the oxide of Reiset's platinum radical, $R'\,O$, $= Pt\,N_2H_6O$, or rather its hydrate $Pt\,N_2H_6O + aq.$ is easily obtained from the sulphate by adding just so much baryta as will remove the sulphuric acid, and evaporating the filtered solution in vacuo, when the hydrated oxide crystallises in colourless needles. This compound is strikingly analogous to hydrate of potash: it is a powerful caustic, attracts carbonic acid from the air as strongly as potash, and exhibits all the chemical characters of one of the strongest alkalies. Few compounds are so remarkable as this base. We shall call it the base *a*.

This singular compound may be viewed as containing the elements of protoxide of platinum, ammonia and water, $Pt\,O$, $2\,N\,H_3$, $H\,O$. When heated to 212°, it loses its water and half its ammonia, leaving a compound $Pt\,N\,H_3O$ or $Pt\,O, N\,H_3$, which appears to be another new base, *b*, combining with acids and forming salts which detonate when heated. This last compound, when heated in the air, burns like tinder, and leaves metallic platinum. It is the oxide of a third radical, *b*, $= Pt\,N\,H_3$.

With hydrochloric acid the base *a* of Reiset yields water and the original chlorine compound, thus: $Pt\,N_2\,H_6, O + H\,Cl = Pt\,N_2\,H_6,\ Cl + H\,O$. When this chloride is heated to from 265° to 290°, it loses ammonia, and there is left a yellow powder, discovered by Peyrone, which dissolves easily in hot water, and has the composition of the green insoluble crystalline compound of Magnus, $Pt\,Cl\,N\,H_3$, of which it is an isomeric modification. Indeed, the compound of Magnus, (although insoluble in hot water,) if boiled with a saturated solution of sulphate or nitrate of ammonia, dissolves and is deposited on cooling in yellow crystals. The yellow ammoniated protochloride of platinum of Peyrone readily dissolves in ammonia, and the solution yields fine colourless prisms of the original chlorine compound of Reiset, but apparently not containing 1 eq. of water of crystallization, which is said to be present in the white scales obtained by Reiset from the green compound of Magnus.

When the yellow compound of Peyrone is acted on by nitrate of silver, it yields chloride of silver, and two new compounds containing nitric acid and platinum, one of which forms yellow octahedrons.

If the sulphate of Reiset's base, $Pt\,N_2\,H_6 + S\,O_4$ be acted on by iodide of barium, Ba I, there is formed sulphate of baryta, $Ba\,S\,O_4$, and a protoiodide of Reiset's radical, *a*, $Pt\ N_2\,H_6, I$. This iodide is soluble and crystallisable, and when boiled with water, loses ammonia, while a new iodine compound is precipitated, $Pt\ N\,H_3\ I$, corresponding to the chlorine compound of Peyrone and to that of Magnus, both of which are $Pt\ N\,H_3\ Cl$.

This new iodine compound seems to be the iodide of the third radical, *b*, $Pt\ N\,H_3$; for when acted on by nitrate or sulphate of silver, it yields iodide of silver, and a nitrate or sulphate of this new radical or of its oxide, $Pt\,N\,H_3, I + Ag, S\,O_4 = Pt\,N\,H_3,\ S\,O_4 + Ag\,I$; and $Pt\,N\,H_3, I + Ag,\ N\,O_6 = Pt\ N\,H_3,\ N\,O_6 + Ag\ I$. These new salts may of course be represented as $Pt\,N\,H_3, O + S\,O_3$, and $Pt\,N\,H_3, O + N\,O_5$. With ammonia, these salts yield the nitrate and sulphate of Reiset's base *a*; and with hydrochloric acid they yield the yellow compound of Peyrone. This would indicate that the latter compound is $Pt\,N\,H_3, Cl$, the chloride of the radical $Pt\,N\,H_3$, while the green salt of Magnus may be the ammoniated protochloride of platinum $Pt\ Cl + N\,H_3$, or probably $Pt\ Cl, N\,H_3 + aq$.

Here we have, at all events, three very remarkable compounds, which contain platinum and the elements of ammonia. There is, first, the radical *b* last described, $Pt\ N\,H_3$; secondly, the radical of Reiset's base, *a*, Pt N_2 H_6; and thirdly, the radical of Gros's base, Pt Cl N_2 H_6.

Now we have given the history of these compounds somewhat minutely, because their existence throws much light on the nature of a numerous and important class of bodies, namely, the vegetable bases or alkaloids.

It will be observed, then, that the three new radicals above described all contain nitrogen, indeed, all contain the elements of ammonia, and are in their chemical relations entirely analogous to ammonium. Thus we have

	Radical.	Oxide.	Chloride.	Sulphate.
Ammonium.	NH_4	NH_4+O	NH_4+Cl	NH_4+SO_4
Radical of Reiset's base *b*	$Pt NH_3$	$Pt NH_3+O$	$Pt NH_3+Cl$	$Pt NH_3+SO_4$
Radical of Reiset's base *a*	$Pt N_2 H_6$	$Pt N_2H_6+O$	$Pt N_2H_6+Cl$	$Pt N_2 H_6+SO_4$
Radical of Gros's base	$PtClN_2H_6$	$PtClN_2H_6+O$	$PtClN_2H_6+Cl$	$PtClN_2H_6+SO_4$

That the above formulæ represent in some respects truly the relation of these new bases to one another, is rendered probable by the fact that, while the radical and base *b* of Reiset differ from his radical and base *a* by containing 1 eq. of ammonia less, and these last from those of Gros by containing 1 eq. of chlorine less, we can actually transform the salts of Reiset's base *b* into those of his base *a*, by the addition of ammonia; and the nitrate of Reiset's base *a*, by the addition of chlorine, yields a salt having the properties of the nitrate of Gros's base.

Now we have seen that ammonium may be viewed as a compound of amide, as $N H_2 + H_2 = Ad H_2$. May we not therefore suppose the new radicals to be also compounds of amide? May not Reiset's radical *b* be ammonium, in which 1 eq. of hydrogen has been replaced by 1 eq. of platinum, $Ad \left\{ \begin{matrix} H \\ Pt \end{matrix} \right.$? Again, just as we have seen in acids, viewed as hydrogen compounds, analogous elements added to the radical without affecting the neutralizing power of the acid, which remains the same as long as the *replaceable* hydrogen continues unchanged, we can suppose amide to be a basic radical, forming with hydrogen the base ammonia, but capable of taking up into the radical analogous elements without affecting the basic character of the ammonia, because we have now the hydrogen compound of an analogous, but more complex, basic radical. On this view, Reiset's radical *b*, may be the hydrogen compound of a basic radical, more complex than amide; in fact, amidide of platinum. Its formula would then be $Ad\ Pt + H$, and, although on this view it should correspond to ammmonia, rather than ammonium, we cannot speak positively, as this is the least known of the three.

The other two radicals may be readily viewed as hydrogen compounds of complex amidides, as ammonium is the hydrogen compound of amidide of hydrogen.

Amide, $N H_2 = Ad$, with hydrogen, forms ammonia $Ad\,H$, and ammonium $Ad\,H + H$. In like manner, in the radical *a* of Reiset's salts, we have a complex amide, composed of amide and amidide of platinum, $Ad + Pt\,Ad = Pt\,Ad_2$, which, with 1 eq. hydrogen, may be supposed to form a compound analogous to ammonia, $Pt\,Ad_2, H$, and with two eq. of hydrogen, actually does form the radical *a* of Reiset, $Pt\,Ad_2\ H + H$, exactly analogous to ammonium. So the radical of Gros may be derived from the complex amide $Pt\,Cl\,Ad + Ad = Pt\,Cl\,Ad_2$, which may form $Pt\,Cl\,Ad_2 + H$ and $Pt\,Cl\,Ad_2\ H + H$, the latter being the actual composition of the radical of Gros, corresponding to ammonium.

It may also be mentioned, that just as we may view ammoniacal salts as containing ammonia and water rather than ammonium and oxygen, so, the base *b* of Reiset may be, $N H_3 + Pt\,O$, analogous to $N H_3 + H\,O$ in the salts of ammonia. If sulphate of ammonia be $N H_3, H\,O + S\,O_3$ the sulphate of Reiset's base *b* will then be $N H_3, Pt\,O + S\,O_3$, the protoxide of platinum here playing the part of water, or in other words, platinum playing the part of hydrogen, a substitution far from unnatural or improbable. Again, if we consider the ammoniaco-sulphate of copper to be $\left.\begin{matrix}2\,N H_3\\ Cu\,O\end{matrix}\right\} + S\,O_3$, then the sulphate of Reiset's base *a* will be $\left.\begin{matrix}2\,N H_3\\ Pt\,O\end{matrix}\right\} + S\,O_3$ where platinum replaces copper, also a not improbable substitution. Reiset is disposed to adopt this view.

The chloride of Gros's radical, $Pt\,Cl\,N_2\,H_6 + Cl$, may be viewed as a compound of bichloride of platinum with ammonia, $Pt\,Cl_2 + 2\,N H_3$, and there is even reason to think that compounds of that radical may be obtained from the solution of bichloride of platinum in ammonia.

From the above remarks it will appear that every probable view which can be taken of these very interesting bases connects them with amide, ammonia, or ammonium, and it is for this reason that they have been treated of in this section. Many pages might be filled with details concerning them: but we have here only indicated those points which will help to elucidate the constitution of the vegetable alkalies.

That important class of compounds not only contains nitrogen, as an essential element, but exhibits the same analogy with ammonia which we have seen to exist in the compound platinum bases. Moreover, like these bases, the alkaloids do not contain ammonia *as such;* and the probability is very great that their constitution is analogous to that of the bases now described.

II. CARBONIC OXIDE (as a Radical); $C_2\,O_2 = 28{\cdot}106$.

Syn.: *Oxalyle.*—There is good reason to believe that the radical of oxalic acid is formed of 2 eq. of carbonic oxide. It has long been known that carbonic oxide, in the sun's light, combines with chlorine to form phosgene gas or chlorocarbonic acid, $C\,O, Cl$ or $C_2\,O_2, Cl_2$. This compound may be viewed as the choride of the radical $C_2\,O_2$, or as carbonic acid, in which 1 eq. of oxygen is replaced by chlorine, $C\left\{\begin{matrix}O\\Cl,\end{matrix}\right.$ corresponding to $C\left\{\begin{matrix}O\\O\end{matrix}\right.$ or $C\,O_2$. But the existence of this radical is more securely inferred from the combinations it forms with oxygen, potassium, and amide.

CARBONIC OXIDE AND OXYGEN.

1. OXALIC ACID $(C_2\,O_2)\,O + H\,O$, or $C_2\,O_4, H = 44{\cdot}132$.

This acid occurs in nature, generally in the form of an acid oxalate of potash in certain vegetable juices, such as that of oxalis acetosella, also as oxalate of lime in many lichens. It is formed artificially by the action of nitric acid on sugar, starch, and many other organic compounds; also by the action of hypermanganate of potash on sugar, &c.

To prepare it, one part of pure starch is gently heated with 8 parts of nitric acid, Sp. G. 1·20 or 1·25. A very energetic reaction ensues, and much nitrous acid is disengaged; when this slackens, heat is applied, and continued till no more red vapours appear, when the liquid, if sufficiently evaporated, deposits, on cooling, a large quantity of crystals of hydrated oxalic acid. These are dried on a porous tile, to remove the mother liquor which contains much free nitric acid, saccharic acid, and other products. The dried crystals being dissolved in a little hot water, the solution, on cooling, deposits pure oxalic acid in four-sided prisms, which are colourless, very acid, very soluble in hot water, moderately so in cold water. These crystals contain 3 eq. of water of crystallisation, $C_2O_3, H\,O + 3$ aq. When sharply heated, a part sublimes as dry acid, $C_2O_3, H\,O$. Oxalic acid is destroyed by heat without blackening, which seems to distinguish it from most other organic acids.

It is very poisonous, and is the cause of many fatal accidents from its similarity to Epsom salts, from which, however, it is easily distinguished by its very sour taste. The best antidote is prepared chalk administered in water, which forms the insoluble and inert oxalate of lime. It is easily detected by forming with lime water, or a soluble salt of lime, if no free acid be present, the very insoluble oxalate of lime, which when dried and heated to low redness is converted, without blackening, into carbonate of lime.

When oxalic acid, or any of its salts, is heated with oil of vitriol in excess, a brisk effervescence takes place, and the gas given off is a mixture of equal volumes of carbonic acid and carbonic oxide. This character furnishes another good means of recognising oxalic acid. The reaction is very simple, for $C_2O_3, HO + HO, SO_3 = (SO_3 + 2HO) + CO + CO_2$. The sulphuric acid seizes the whole of the water, and the anhydrous oxalic acid, C_2O_3. cannot exist in the separate state.

When the oxalates of certain protoxides, as those of cobalt and nickel, are heated in close vessels, the metal is left; carbonic acid being given off; $Co O, C_2O_3 = Co + 2CO_2$. Other oxalates, as that of manganese, give off carbonic acid and carbonic oxide, leaving the protoxide of the metal, $Mn O, C_2O_3 = Mn O + CO + CO_2$.

Oxalic acid forms salts with bases, many of which are insoluble. The insolubility of the oxalate of lime renders oxalic acid useful as a test for lime, and as a means of separating it, and determining its quantity, in analysis. As a test, it is commonly used in the form of oxalate of ammonia. It can only detect lime in neutral or alkaline fluids, the oxalate of lime being soluble in free acids.

The formation of oxalic acid by the action of oxidising agents on organic matters, is a partial oxidation of their carbon; when that oxidation is complete, carbonic acid is the result. The action of nitric acid on starch or sugar is complicated, and not so well understood as to admit of being expressed in the form of an equation; but the oxidation of sugar by permanganate of potash is very simple, and is thus represented, $C_{12}H_{10}O_{10} + 6(KO, Mn_2O_7) = 6(KO, C_2O_3) + 10HO + 12MnO_2$; that is, 1 eq. of anhydrous sugar, with 6 eq. of the permanganate, produces 6 eq. of oxalate of potash, 10 eq. of water, and 12 eq. of peroxide of manganese.

The most important oxalates are those of potash, lime and ammonia. There are three oxalates of potash; the neutral oxalate, $K O, C_2O_3 + aq.$; the binoxalate, $K O, C_2O_3 + H O, C_2O_3 + 2 aq.$; and the quadroxalate, $K O, C_2O_3 + 3 (H O, C_2O_3) + 4 aq.$ The oxalate of lime is $Ca O, C_2O_3 + 2 aq.$ The oxalate of silver $Ag O, C_2O_3$, detonates when heated, yielding, like several other oxalates of the noble metals, carbonic acid, and the metal. The oxalate of ammonia, $N H_4O, C_2O_3 + aq.$ is much used as a test. It crystallises very readily. When heated, it gives rise to a very remarkable compound, namely *oxamide*, which is the type of a class. We shall here consider it.

Oxamide, $C_2H_2 NO_2 = C_2O + NH_2 = 44{\cdot}296$.

When oxalate of ammonia is heated in a retort, it gives rise to a variety of products, and among these, to a white crystalline powder, insoluble in cold water, which is oxamide. It may be formed far more abundantly by the action of ammonia in solution on oxalate of oxide of ethyle, or oxalic ether. (See oxalate of oxide of ethyle.)

The remarkable character of oxamide is, that while itself neutral, and certainly containing neither oxalic acid nor ammonia, it is easily converted into oxalic acid and ammonia by boiling it either with strong acids or strong alkalies. In this reaction, the elements of 1 eq. of water are shared between the constituents of oxamide, that is, between the radical $C_2 O_2$ and the radical amide, $N H_2$; for oxamide is nothing more than oxalate of ammonia, $N H_4O, C_2O_3$, minus 2 eq. of water, or $N H_2, C_2O_2$. A very small portion of an acid, for example, is sufficient to produce this effect on a large quantity of oxamide; for if the acid we add be neutralised by the ammonia produced, a corresponding quantity of oxalic acid is set free, and acts as any other acid would do. A minute proportion of an acid, therefore, here, appears to exert its influence on an unlimited portion of oxamide, but this is only in appearance. The fact, however, that the presence of a little oxalic acid enables oxamide to decompose water and to produce ammonia and oxalic acid, is very important, and tends to throw light on many similar changes in the organic kingdom, where the agency is not so apparent.

But oxamide is not the only product of the action of heat on oxalate of ammonia; for, besides carbonic acid, carbonic oxide, hydrocyanic acid, water, ammonia, and oxamide, all of which are or may be formed, there is produced, when the heat is so regulated that a honey yellow residue remains in the retort, a new acid, called oxamic acid, which constitutes that residue. It is mixed with a little oxamide, which is, however, left undissolved by hot water, in which the oxamic acid dissolves.

Oxamic acid forms soluble and crystallisable salts with lime, baryta, ammonia and oxide of silver. Acids precipitate it from the saturated solution of its compound with ammonia, as a white sparingly soluble powder, the composition of which is $C_4H_2NO_5+aq$. Although an acid, this compound exhibits all the relations of a compound of amide or amidogen, being converted by the action of alkalies at a high temperature into oxalic acid and ammonia. It differs, however, from oxamide in yielding 2 eq. oxalic acid and 1 eq. ammonia; for 1 eq. of oxamic acid, *plus* 3 eq. of water, contains the elements of binoxalate of ammonia. $C_4O_5, NH_2+3\ HO=(HO, C_2O_3)+(NH_4O, C_2O_3)$. This also explains its production;—

for 2 eq. Oxalate of Ammonia $2\ (NH_4O, C_2O_3)=C_4H_8N_2O_8$
when acted on by heat,
Yield 1 eq. ammonia $= H_3N$
3 eq. water $= H_3\ O_3$
1 eq. anhydrous oxamic acid $=C_4H_2N\ O_5$

Together . . . $C_4H_8N_2O_8$

Oxamic acid is certainly a very remarkable compound, being an acid amidide, or at least admitting of being so regarded, C_4O_5, NH_2. There are a few other examples of acid amidides, and we shall soon come to one, namely, *euchronic acid*, which is highly analogous to oxamic acid: being formed by the action of heat on mellitate of ammonia, along with a neutral amidide, *paramide*, similar to oxamide; and as oxamic acid yields acid oxalate, so euchronic acid yields acid mellitate of ammonia when long boiled with water. Cyanic acid may also be considered as, in some sense, an acid amidide; for $C_2NO, HO=C_2O_2, NH$; and $C_2O_2, NH+2HO=NH_3, 2\ CO_2$; or, as is well known, cyanic acid, in contact with water, produces bicarbonate of ammonia.

Oxamic acid may further be viewed as a coupled oxalic acid, the adjunct in which is oxamide: for $C_4\ O_5NH_2$ is equal to $C_2O_3+C_2O_2, NH_2$. Berzelius adopts this view, and is, generally speaking, favourable to the idea of coupled acids.

By the action of chlorocarbonic acid on alcohol, an ether is formed, which, with ammonia, yields a very beautifully crystallisable compound, long known as oxamethan, which is nothing else than oxamate of oxide of ethyle (see salts of oxide of ethyle). Its composition is $C_8H_7NO_6=(C_4H_5)O+C_4H_2NO_5$. A similar compound exists with oxide of methyle, and was formerly called oxamethylan.

2. Carbonic Acid. $CO_2 = 22$.

This acid has been already described, and it is introduced here merely because it is formed by the complete oxidation of carbonic oxide; $C_2O_2 + O_2 = 2\,CO_2$.

CARBONIC ACID AND CHLORINE.

Chlorocarbonic Acid. $C\left\{\begin{matrix}O\\Cl\end{matrix}\right.$ or $CO + Cl = 49{\cdot}5$.

Syn. *Phosgene gas.* When equal volumes of chlorine and carbonic oxide are mixed and exposed to the sun's rays, they combine to form a colourless gas, of a pungent disagreeable smell, which acts strongly on the eyes. Sp. G. of the gas 3·399. When dissolved in water, it decomposes it, producing carbonic and hydrochloric acids. With alcohol and pyroxilic spirit it produces very remarkable compound ethers, to be afterwards described.

With ammonia, this acid forms sal ammoniac, and a white volatile crystalline substance, which is carbamide, CO, NH_2, produced as follows:—$CO, Cl + 2\,NH_3 = NH_4, Cl + CO, NH_2$

Under the influence of the mineral acids, carbamide yields ammonia and carbonic acid, $CO, NH_2 + HO = CO_2 + NH_3$.

The chlorocarbonic acid may be considered as carbonic acid $C + \left\{\begin{matrix}O\\O,\end{matrix}\right.$ in which half the oxygen has been replaced by its equivalent of chlorine, $C + \left\{\begin{matrix}O\\Cl.\end{matrix}\right.$

CARBONIC OXIDE WITH POTASSIUM.

Oxycarburet of Potassium: Rhodizonic Acid.

When potassium is heated in carbonic oxide gas, combination takes place, and a dark olive powder is formed, composed of carbonic oxide and potassium, in the proportions of $C_7O_7 + K_3$, or $7\,CO + 3\,K$. This substance is formed in large quantity in the preparation of potassium from carbonate of potash and charcoal, and is the source of great loss as well as inconvenience. No such compound is formed with sodium, for which reason that metal may be more cheaply prepared than potassium.

The oxycarburet of potassium, if heated in the air, takes fire, but if exposed to moist air, or placed in water, it is converted into the potash salt of a new acid, rhodizonic acid, hydrogen being disengaged, $C_7O_7K_3 + 3\,HO = C_7O_7, 3\,KO + H_3$. As this hydrogen, however, is not pure, but contains carbon, the reaction is probably more complicated.

All the salts of rhodizonic acid are deep red, and when in crystals, reflect a green light. The rhodizonate of potash, when heated in solution in water, undergoes a very remarkable change, yielding free potash, oxalate of potash and croconate of potash, the latter being the salt of another new acid containing the same elements as rhodizonic acid in different proportions; this salt is C_5O_4,KO or C_5O_5,K. The composition of rhodizonate of potash explains this re-action perfectly, for $C_7O_7+3KO=KO+KO,C_2O_3+KO,C_5O_4$.

Croconic Acid. $C_5\,O_4$, HO? or $C_5\,O_5$, H.

This acid is named from the yellow colour of its salts. It is obtained from the croconate of potash, prepared as above, by the action of fluosilicic acid, which separates the potash. The acid is yellow, soluble in water and alcohol, and crystallises easily. All its salts are likewise yellow.

The rhodizonic acid, $C_7\,O_7$, 3 HO, may be viewed as a tribasic hydrogen acid, $C_7\,O_{10}$, H_3; the croconic acid may also be viewed both as a hydrated oxygen acid, $C_5\,O_4$, HO, and as a hydrogen acid, $C_5\,O_5$, H. In this last form it connects itself with carbonic oxide, as it may be $5\,CO+H$. The same remark applies to another remarkable acid, containing the same elements, namely the mellitic acid.

Mellitic Acid. C_4O_3, HO or $C_4\,O_4$, H.

This acid occurs, combined with alumina, in a very rare mineral, probably of organic origin, the mellite or honey-stone. The acid is soluble, very sour, and permanent, not being altered by boiling nitric or sulphuric acids, nor by a heat of nearly 580°. The general formula of its salts, when dried at 212°, is MO, $C_4\,O_4$ H, or HO, $C_4\,O_4$ M. The salt of silver, however, at 212°, loses 1 eq. of water, and is left as $C_4\,O_3$, Ag O, or $C_4\,O_4$, Ag. According to the latter formula, the radical in this salt, heated to 212°, is a form of carbonic oxide, $C_4\,O_4=4\,CO$.

The crystallised acid $C_4\,O_3$, HO, or $C_4\,O_4$H, appears to unite with most bases without the separation of water, generally observed when salts are formed. And although the silver salt would seem to contain a different radical, yet it yields, when decomposed, the original mellitic acid.

The mellitate of silver may also be looked on as oxalate of silver Ag O, $C_2\,O_3$, plus 2 eq. of carbon in the acid Ag O, $C_4\,O_3$.

The mellitate of ammonia, NH_4 O, $C_4\,H_3$, when heated in a retort, yields several new and remarkable products. When this salt, NH_3, HO, $C_4\,O_3=C_4\,H_4\,NO_4$ is heated to 320°, it gives off ammonia and water, and there remains a mixture of two new compounds; a soluble one which contains *euchronic acid,* in combination with ammonia, and an insoluble one which is called *paramide.*

Paramide is a yellow solid, like clay. Its most remarkable character is that, when long boiled with water, it is converted into bimellitate of ammonia. This is the character of an amide, hence its name. The composition of paramide is $CHNO_4$, which readily explains, both its formation, and its conversion into bimellitate of ammonia.

If from bimellitate of ammonia, $NH_4O, C_4O_3 + HO, C_4O_3 = C_8H_5NO_8$
we subtract 4 eq. of water . . . . $H_4\ \ O_4$

there will remain . . . . . . Paramide $= C_8H\ \ NO_4$

and of course, when reconverted into bimellitate of ammonia by long boiling, it merely takes up again these 4 eq. of water.

The soluble compound, euchronate of ammonia, when its solution is acted on by hydrochloric acid, deposits a white crystalline powder, which is euchronic acid, $C_{12}NO_6, 2HO$. Its formation is easily explained; for

if from 3 eq. of mellitate of ammonia $= 3(C_4H_4NO_4) = C_{12}H_{12}N_3O_{12}$
we subtract 6 eq. water and 2 eq. ammonia $= H_{12}N_2O_6$

there will remain anhydrous euchronic acid $= C_{12}\ \ NO_6$

We can now see that the action of heat on 7 eq. of mellitate of ammonia gives rise to the following substances:—

2 eq. Paramide $= C_{16}H_2N_2O_8$
1 eq. Euchronic Acid $= C_{12}\ \ NO_6$
4 eq. Ammonia $= H_{12}N_4$
14 eq. Water $= H_{14}\ \ O_{14}$

7 eq. mellitate of ammonia $= C_{28}H_{28}N_7O_{28}$

When euchronic acid is boiled with water, it is dissolved and converted into an acid mellitate of ammonia.

1 eq. Euchronic Acid $= C_{12}\ \ NO_6$
and 6 eq. Water $= H_6\ \ O_6$

Together . . $C_{12}H_6NO_{12}$ are equal to

3 eq. Mellitic Acid $= C_{12}H_3\ \ O_{12}$
and 1 eq. Ammonia $= H_3N$

Together . . $C_{12}H_6NO_{12}$

Euchronic acid is deoxidised by a plate of zinc, yielding a powder of a fine deep blue colour, which dissolves in ammonia or potash, with a splendid tint of purple. The blue powder is an inferior oxide of the same nitrogenised radical, which, combined with more oxygen, forms euchronic acid. The whole subject of mellitic acid and euchronic acid is most interesting, but mellitic acid is so rare that it is very difficult to find material for the investigation. As mellitic acid, like succinic acid, is of organic origin, and contains only 1 eq. of hydrogen less, and 1 eq. of oxygen more than succinic acid, we may hope to be enabled to obtain it artificially.

III. Cyanogen. $C_2N = Cy = 26{\cdot}23$.

This very important compound has already been mentioned as a compound of carbon and nitrogen; but we have now to consider it in its far more important character of a compound radical. In fact, it was the first compound radical discovered, and the discovery of cyanogen by Gay-Lussac has proved more fertile in results than any other discovery yet made in Organic Chemistry. As cyanogen acts exactly like an element, we shall represent it by the symbol Cy, rather than by C_2N; using the latter only where the elements of cyanogen, and not itself, enter into changes and reactions.

Cyanogen is formed when animal matter is ignited along with carbonate of potash in close or covered iron vessels. The cyanogen being a gas, and combustible, would be dissipated, and in open vessels burned, were it not that it enters into combination with potassium derived from the carbonate, forming cyanide of potassium, KCy, a salt not altered by a red-heat in close vessels. As this salt, however, is decomposed by the action of water, yielding carbonate of potash and of ammonia, hydrogen being set free, ($K, C_2N + 5\,HO = KO, CO_2 + NH_3, HO, CO_2 + H$), it is necessary to convert the cyanide of potassium into a more stable compound. This is effected by the addition of iron, or of sulphuret of iron, the latter of which is formed by the mutual action of the sulphate of potash (always present in potashes), carbon, and the iron of the vessel. The iron, or its sulphuret, is readily dissolved by the aqueous solution of cyanide of potassium, yielding cyanide of iron, $Fe\,Cy$, and sulphuret of potassium KS, for $KCy + Fe\,S = Fe\,Cy + KS$. The elements of the cyanide of iron then form, with cyanide of potassium, the very permanent double cyanide, well-known as prussiate of potash, properly ferrocyanide of potassium, which forms large and pure, transparent, yellow crystals. From this compound, all the other compounds of cyanogen, and cyanogen itself, are prepared. Its empirical formula is $Fe\,Cy, 2\,KCy + 3\,HO$, or $Fe\,K_2\,Cy_3 + 3\,HO$. At 212° it loses all the water, and then contains only iron, potassium, and cyanogen $Fe + K_2 + Cy_3$. It may be conveniently viewed as a compound of cyanide of iron with cyanide of potassium; but we shall see hereafter that its rational formula is probably very different, and that it is a compound of potassium with a new radical, ferrocyanogen.

Cyanogen gas is best prepared by heating dried bicyanide of mercury, when the gas is given off, a part, however, assuming the solid form, and remaining behind as a black matter, paracyanogen, isomeric with cyanogen : or by heating a mixture of 6 parts dried ferrocyanide of potassium, and 9 parts bichloride of mercury, when chloride of potassium is formed by the action of the bichloride on the cyanide of potassium of the ferrocyanide, and the cyanide of mercury, if formed, is at once decomposed by the heat. $Fe\,Cy, 2\,K\,Cy + Hg\,Cl_2 = Fe\,Cy, 2\,K\,Cl + Hg + Cy_2$. The cyanide of iron is not altered. The gas may be collected over mercury, but is absorbed by water, with which it produces the various changes which have been minutely explained at pp. 26 and 27. It has a very pungent and peculiar smell, is colourless and transparent; and may be liquefied by a pressure of about 4 atmospheres. It is combustible and burns with a beautiful pink or purplish flame.

Cyanogen forms with hydrogen an acid, the hydrocyanic, $H\,Cy$; with oxygen and the elements of water, three acids, $Cy\,O, H\,O$; $Cy_2\,O_2, 2\,H\,O$; and $Cy_3\,O_3, 3\,H\,O$; of which the first is cyanic, the second fulminic, and the third is cyanuric acid. With chlorine, &c. it combines; with sulphur it forms a new radical $Cy\,S_2$, sulphocyanogen; and with metals it forms salts, perfectly analogous with chlorides, such as $K\,Cy$, $Fe\,Cy$, $Ag\,Cy$, $Hg\,Cy_2$, &c. In short it plays exactly the part of a simple radical, and were it not easily decomposable, we should at once class it with chlorine as an element.

CYANOGEN AND HYDROGEN.

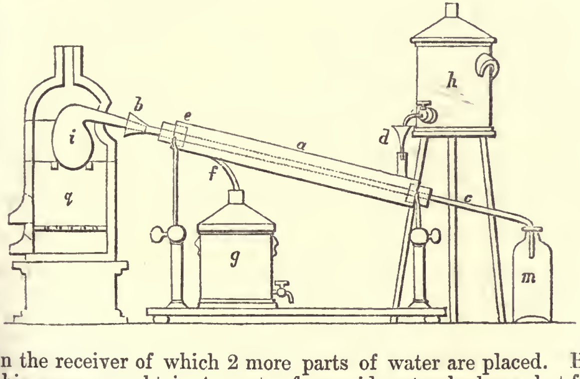
Hydrocyanic or Prussic Acid. $H\,Cy = 27{\cdot}23$.

This acid may be obtained by a great variety of processes; but the easiest, most economical, and most certain, is to act on the ferrocyanide of potassium with diluted sulphuric acid. The process requires to be slightly modified, according as our object is to prepare the dry or anhydrous acid, or the diluted aqueous solution of it used in medicine.

1. *Anhydrous Acid.*—To prepare this acid, 15 parts of powdered ferrocyanide are to be distilled at a gentle heat with a mixture of 9 parts of oil of vitriol, and 9 of water, and the product is to be received in a convenient receiver placed in a freezing mixture, and containing 5 parts of chloride of calcium in small lumps. As soon as liquid enough has distilled to cover the chloride, the distillation is stopped, and the hydrocyanic acid, deprived of water by the chloride of calcium, is to be decanted into a dry and well-stopped bottle. It may also be obtained by distilling, under similar circumstances, cyanide of

potassium with dilute sulphuric acid. In both cases, the acid is formed by the reaction of sulphuric acid on cyanide of potassium, or its elements. $KCy+H, SO_4=K, SO_4+HCy$. Dry hydrocyanic acid is a limpid and colourless liquid, of Sp. G. 0·6967 at 66°; at 59° it becomes a fibrous mass, in consequence of the presence of a trace of water; and at 80° it boils; the density of its vapour is 0·9476. It is inflammable, and has a very peculiar and disagreeable smell and taste. It is the most energetic poison known, one drop introduced into the mouth being sufficient to destroy an animal of considerable size. When pure it is soon spontaneously decomposed, depositing a dark brown solid; a trace of sulphuric acid causes it to keep perfectly. When in contact with the strong mineral acids and water, it is decomposed, being converted into ammonia and formic acid; $H, C_2 N+4 HO=NH_3, HO+C_2 HO_3$.

2. *Medicinal or diluted Hydrocyanic Acid.*—This may be prepared by simply diluting the anhydrous acid with the required proportion of water, adding, for example, 97 grains of water to 3 of the acid, to obtain an acid of 3 per cent.; which is about the average strength used in medicine. In round numbers, to 1 part, *by weight*, of dry acid, $32\frac{1}{3}$ parts of water, by weight, are to be added; or, to 1 *volume* of anhydrous acid, $22\frac{1}{2}$ volumes of water. But as it is troublesome to prepare the anhydrous acid, it is best to distil 2 parts of ferrocyanide, with 1 of sulphuric acid and 2 of water, to dryness in a chloride of calcium bath, condensing in a Liebig's apparatus, in the receiver of which 2 more parts of water are placed. By this means we obtain $4\frac{1}{2}$ parts of an acid, not anhydrous, but far too strong for use, containing from 15 to 20 per cent. of dry



acid. Its precise strength is ascertained, and it is reduced to the standard strength, in the following simple manner :—

Any convenient quantity, say 50 or 100 grains, is weighed out, being added to a counterpoised vessel containing about 2 drachms of nitrate of silver, dissolved in 2 or 3 ounces of water. Let us suppose that we have dropped into this vessel 70 grains of our acid. This will be entirely converted into cyanide of silver, but we make sure by testing with a drop of nitrate of silver. The precipitate is then collected on a filter, well washed, dried at 212° on a weighed filter, and the increase in weight of the filter gives the weight of the cyanide of silver formed. Now this cyanide is formed as follows : $HCy + (AgO, NO_5) = AgCy + (HO, NO_5)$. Therefore, 1 eq. of hydrocyanic acid, $HCy = 27{\cdot}23$ produces 1 eq. cyanide of silver $AgCy = 134{\cdot}54$; or 1 grain of anhydrous hydrocyanic acid will yield almost exactly 5 grains of cyanide of silver ; for 27·23 : 134·54 : : 1 : 4·94. We may, therefore, safely assume that the weight of the cyanide of silver, divided by 5, gives the weight of anhydrous acid present with sufficient accuracy for all practical purposes. Now, we have used 70 grains of our dilute acid, the strength of which we wish to know. Let us suppose that our filter weighs, when empty, 20 grains, and with the cyanide of silver, dried at 212° till it ceases to lose weight, 100 grains. The difference, or 80 grains, is the weight of cyanide of silver obtained from 70 grains of our acid. Dividing this by 5, we have 16 grains as the weight of anhydrous acid contained in the 70 grains, and consequently combined with 54 of water.

Now, if we wish to state the per centage of this acid, we obtain it by the calculation, 70 : 16 : : 100 : x, and $x = \frac{16 \times 100}{70} = 22{\cdot}85$, so that our acid contains 22·85 per cent. of anhydrous acid. But if our only object be to reduce the acid to a standard strength, say that of 3 per cent., this last calculation is unnecessary, and we can proceed as follows : acid of 3 per cent. contains 3 grs. of dry acid and 97 of water ; therefore, to find how much water is to be added to 16 grs. of anhydrous acid, 3 : 97 : : 16 : x, and $x = \frac{97 \times 16}{3} = 517{\cdot}3$ grains of water, which must be added to 16 grs. of anhydrous acid, to bring it to the same strength. But our 70 grains of acid contain already, with the 16 of anhydrous acid, 54 grains of water, consequently we have only to add to these 70 grains 517·3 — 54 = 463·3 grains of water, and the same quantity of water for every 70 grains of the same acid. Of course, it is easy to calculate the water necessary for 1 or more ounces of the acid, when we have once found it for any given quantity. I have here supposed 70 grains, but with 50 or 100 the calculation is easier, and with a drachm by weight (60 grains), we have simple data for calculating how much water is required for any number of ounces or drachms of acid.

This beautiful and simple method of preparing the medicinal hydrocyanic acid, and ascertaining its precise strength, has been minutely described, because of its practical importance. It is so simple an operation, that any one may very soon learn to ascertain the strength of hydrocyanic acid, and it is very exact. Besides, no other method of obtaining a medicinal acid of uniform strength ought to be trusted to; and we ought never to attempt to obtain the acid of the standard strength by distillation, although many methods are given for this. I have never seen any one of these yield twice the same result; whereas by the above method we can prepare acid of exactly the same strength any number of times, and the acid prepared from the ferrocyanide, by sulphuric acid, keeps perfectly well. Of course, when we have added the calculated quantity of water to reduce the acid, it is proper to ascertain its strength once more, to make sure that we have made no error in our calculation. If it be acid of 3 per cent., it will yield 15 grains of cyanide of silver from 100 of acid.

There are two other methods which deserve to be mentioned, as, with pure materials and careful manipulation, they yield, in a few minutes, a standard acid. The first is that of Dr. Clarke, who adds to 1 eq. cyanide of potassium dissolved in water, 2 eq. Tartaric acid, which separates the potassium as cream of tartar, while diluted hydrocyanic acid remains dissolved. For every 100 grs. of water, 7⅓ grs. of cyanide of potassium and 16½ of crystallised Tartaric acid, are required. This is an excellent extemporaneous process, if we have pure cyanide of potassium, but that salt does not keep well, and even in its preparation it is apt to be decomposed, at least, partially. It is, besides, an expensive salt. The other is the process of Everett, who suspends cyanide of silver in water, and adds an equivalent of hydrochloric acid. $\text{Ag Cy} + \text{H Cl} = \text{Ag Cl} + \text{H Cy}$. This is also a good extemporaneous process, 15 grs. of Ag Cy being used for every 100 of water, and 4 grs. of dry HCl, that is, about 12 grs. of acid Sp. G. 1.21, being added. This process is also expensive, although the silver is not lost; but the chief objection is, that it is difficult to add the precise amount of hydrochloric acid which is necessary, and that an excess causes, *pro tanto*, a conversion of the hydrocyanic acid into formic acid and ammonia.

The medicinal acid has the smell and taste of the anhydrous, and is very poisonous, the average dose safe for an adult being 1 to 2 drops in a glass of water. It is much used as a sedative and anodyne, but, unless its strength and dose be perfectly known, it is a dangerous remedy. Fatal accidents have occurred from prescriptions, found, after experience, to act favourably, being made up in another place, or by the same druggist with a fresh stock; this fresh stock being exactly of the standard strength, while the previous acid had lost so much by keeping that the dose had been of necessity increased. There, danger actually arose from a too weak acid being used. Hence the necessity for the great exactness, for which rules are given above. In cases of poisoning by this acid, now unfortunately of very frequent occurrence, there is seldom time to administer an antidote; but when life is not extinct, we may confidently rely on the antidotes we possess. The best is the administration of two solutions, one of mixed sulphate of protoxide and peroxide of iron, and the other of carbonate of potash, as recommended by Messrs. Smith, Edinburgh,* by which the acid still in the stomach is rendered insoluble, being converted into Prussian blue. The symptoms already produced are best combated by ammonia inspired from a sponge, or taken, diluted, internally, and by other diffusable stimulants; also by the cold affusion.

Hydrocyanic acid is very easily recognised by its smell, and by its forming Prussian blue if acted on, in solution, successively, by proto-persulphate of iron, by potash, and by an excess of hydrochloric acid. The first two tests form the Prussian blue, the last, dissolving the excess of oxide of iron, brings the blue into view. Any liquid, suspected to contain hydrocyanic acid, ought first to be distilled with the addition of a little dilute sulphuric acid, and the tests applied to the first ounce that comes over. Nitrate of silver produces a white cloud of cyanide of silver, exactly like the chloride in appearance.

Hydrocyanic acid, with metallic oxides, gives rise to water and metallic cyanides. $HCy + MO = HO + MCy$: or $2\,HCy + MO_2 = 2\,HO + MCy_2$.

CYANOGEN AND OXYGEN.

1. Cyanic Acid. $CyO, HO = CyO_2, H = 43{\cdot}25$.

A monobasic acid; is formed when dry cyanide of potassium is heated in the air, when oxygen is absorbed, and cyanate of potash is produced. $KCy + O_2 = KO, CyO$ or K, CyO_2.

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* See *Lancet* for 1844, Vol. II. p. 41.

When a stronger acid is added to this salt, the cyanic acid is set free, but immediately decomposes with water, producing ammonia which unites with the strong acid used, and carbonic acid which escapes as gas. $C_2 NO, HO + 2HO = NH_3 + 2 CO_2$. The carbonic acid carries with it a little cyanic acid, which forms dense white vapours, and has a pungent acid smell like that of strong acetic acid. Under all circumstances, free cyanic acid, in contact with water, is instantly destroyed.

It may, however, be obtained in the anhydrous state, according to the formula $Cy\ O_2 + H$, or as monohydrated acid, if viewed as $Cy\ O, H\ O$, by distilling cyanuric acid, $Cy_3O_6 + H_3$, or $Cy_3O_3 + 3\ H\ O$. This acid is isomeric with cyanic acid, and, when heated, 1 eq. cyanuric acid splits up into 3 eq. cyanic acid, which appears in the receiver as a volatile, pungent, very corrosive acid liquid. This acid only keeps for a very short time, even in the freezing mixture in which it is condensed. If removed from the cold, it soon becomes turbid, then hot, boils violently and with violent shocks, and is converted into a solid dense white body, like porcelain, quite insoluble and indifferent.

This is *Cyamelide*, another isomeric compound, containing the same elements in the same proportions, but differently arranged, possibly $C_2O_2 + N\ H$; for it yields, under the influence of water and strong acids, carbonic acid and ammonia, (C_2O_2, $N\ H + 2\ H\ O = 2\ C\ O_2 + N\ H_3$) just as cyanic acid does. When distilled, it is reconverted into cyanic acid, another proof that it is isomeric with that acid.

CYANATES.

The salts of cyanic acid are all distinguished by the action on them of strong acids, which cause disengagement of carbonic acid, while ammonia may now be detected in the liquid. The cyanates of potash, ammonia, &c. are soluble, those of lead, silver, &c., insoluble,

Cyanate of potash is best formed by the oxidation of Liebig's cyanide of potassium,* which may easily be effected by adding litharge in proper quantity to the melted salt, $K\ Cy + 2\ Pb\ O = K, Cy\ O_2 + Pb_2$. The cooled mass is powdered and boiled with alcohol of 80 per cent., which on cooling deposits pure crystals of cyanate of potash, very similar to chlorate of potash. Or dried ferrocyanide of potassium, mixed with half its weight of peroxide of mangenese, may be gently heated, spread out on an iron plate, when it burns like tinder, partly at the expense of the oxide of manganese, partly in the oxygen of the air. It is well stirred till every part has glowed, and the cold mass is treated with alcohol as above.

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* The formation of this salt will be described below.

Cyanate of potash must be kept in sealed tubes, for in phials occasionally opened it is soon changed into bicarbonate of potash, ammonia being given off. $K, C_2NO_2 + 3HO = (KO_1\ 2CO_2) + NH_3$: Triturated with dried oxalic acid, this salt yields oxalate of potash and cyamelide. When acetic acid is added to a concentrated freshly made solution of cyanate of potash, the latter being in excess, there is deposited the acid cyanurate of potash,

$$Cy_3O_6 \begin{cases} K \\ H_2 \end{cases} \text{ or } Cy_3O_3 \begin{cases} KO \\ 2\,HO \end{cases}$$

CYANATE OF AMMONIA.

a. *basic.* When dry ammonia and the vapour of cyanic acid are mixed, they form a light white solid, which is a cyanate of ammonia, containing more ammonia than is required for a neutral salt. This salt gives off ammonia when treated with alkalies, and cyanic acid when treated with sulphuric acid. But if dissolved in water, and the solution digested and evaporated, it yields crystals, which, although containing the elements of cyanic acid, ammonia, and water, exhibit neither of these characters of a cyanate, but are found to possess all the properties of *urea*, a product of the animal system.

b. *anomalous cyanate of ammonia*, or urea, $C_2H_4N_2O_2 = (C_2NO, HO, NH_3)$. This remarkable compound exists in large proportion in healthy urine, and is extracted from it by evaporating at about 200° to a thin syrup, and adding about an equal volume of colourless nitric acid, Sp. G.1.35, quite free from nitrous acid, which forms a very copious crystallization of nitrate of urea, while the colouring matter is destroyed with brisk effervescence. If cold be applied, the colouring matter resists, and the nitrate is then very dark and very difficult to purify; cold ought therefore, not to be used, and the nitrate of urea is deposited nearly white, having only a clear yellow tint. It is dissolved in water, after being recrystallised, and neutralised by potash or baryta. The whole is then gently evaporated to dryness, after separating as much nitrate of potash or of baryta as possible, and the dry mass digested in alcohol, which dissolves only the urea, and by spontaneous evaporation yields it in large transparent prismatic crystals. Should these not be colourless, the digestion of their aqueous solution with a little permanganate of potash, which has no action on urea, destroys the colouring matter entirely. Should an excess of that salt be added, a few drops of alcohol will instantly destroy it, and the filtered liquor will yield snow-white crystals of urea.

But although urea may thus be obtained (or by the action of oxalic acid on the urine, which forms a sparingly soluble oxalate of urea) in any quantity from urine, it is found much easier to prepare it artificially from cyanate of ammonia. Liebig recommends the following process, which I have found to succeed perfectly. 28 parts of dried ferrocyanide of potassium, and 14 of peroxide of manganese are mixed in powder and calcined, as above described, on a flat iron plate at a very low red heat, sufficient to keep up the glow which takes place. When this is over, the cold mass, powdered, is acted on by a moderate quantity of cold water, which dissolves the cyanate of potash. This is filtered off, and set aside. A fresh portion of cold water being added to the powder, to wash it, is also filtered, and in this liquid are now dissolved 20½ parts of sulphate of ammonia, and the solution is added to the first filtered solution of the cyanate. A large quantity of sulphate of potash is deposited, which is strained off, and the filtered liquid now containing, with some sulphate of potash, all the cyanate of ammonia, is evaporated to dryness, during which process the cyanate of ammonia is transformed into urea. The dry mass is digested in alcohol, which dissolves only the urea, and yields it from the first chemically pure and in any quantity, if the operation be carefully performed. Urea thus obtained is far cheaper than that extracted from urine.

The artificial production of urea from cyanate of ammonia, was discovered by Wöhler. It was the first example of an organic product artificially formed, although many other cases are now known.

Urea forms 4-sided prisms, resembling nitre in appearance, and also in their taste, which is saline and cooling, exactly like that of nitre. It is soluble both in water and alcohol. When heated, it melts, gives off much ammonia, and finally solidifies, being in a great measure converted into ammonia and cyanuric acid.

Urea belongs to the class of organic bases, for it forms crystallisable compounds with several acids, such as nitric, oxalic, and acetic acids.

The nitrate, when impure, crystallises in scales of a high lustre; when pure, it forms opaque prisms, or a crystalline powder. It is sparingly soluble in cold water, but very soluble in hot water. Formula, $(C_2\,H_4\,N_2\,O_2, HO, NO_5)$.

The oxalate forms long transparent prisms, very sparingly soluble. Formula, $(C_2\,H_4\,N_2\,O_2, HO, C_2\,O_3) = C_4\,H_5\,N_2\,O_6$.

The acetate I have obtained as a mass of prismatic crystals, exceedingly soluble in water. Formula, probably $(C_2\,H_4\,N_2\,O_2, HO, C_4\,H_3\,O_3) = C_6\,H_8\,N_2\,O_6$.

Although urea combines with pure nitric acid, it is instantaneously decomposed by hyponitrous acid, yielding ammonia, water, and equal volumes of carbonic acid and nitrogen gases. $C_2\,H_4\,N_2\,O_2 + NO_3 = NH_3 + HO + 2\,CO_2 + N_2$. When acted on by strong acids, or alkalies, with the aid of heat, urea takes up the elements of water, and forms carbonate of ammonia, $C_2\,H_4\,N_2\,O_2 + 2\,HO = 2\,(NH_3, CO_2)$. When urine is left in contact with the mucus usually suspended in it, the mucus entering into decomposition excites in the urea such a reaction with the elements of water, as very soon to convert the whole urea into carbonate of ammonia. Hence the reason why urine soon becomes alkaline, even if acid when voided. But if filtered from the mucus as soon as passed, it keeps unchanged, in clean vessels, for a long period.

2. Fulminic Acid. $Cy_2\,O_2, 2\,HO = Cy_2\,O_4, H_2 = 86{\cdot}5$.

A bibasic acid, unknown in the separate form. It is obtained in combination with oxide of mercury, or oxide of silver, by treating alcohol with the nitrates of these metals, and free nitric acid. A violent effervescence takes place, dense white vapours are disengaged, and a crystalline powder is deposited, which is fulminate of mercury or of silver. Both detonate powerfully by heat, friction, or percussion.

In the above re-action there are first formed, on the one hand, hyponitrous acid; on the other, aldehyde, and formic and oxalic acids. The fulminic acid is the result of a reaction between oxide of ethyle (ether) and hyponitrous acid, in presence of oxide of mercury or oxide of silver. $2\,NO_3 + (C_4\,H_5)\,O = C_4\,N_2\,O_2 + 5\,HO = Cy_2\,O_2, 2\,HO + 3\,HO$.

This acid cannot be isolated, being instantly decomposed when deprived of a fixed base. It forms two series of salts: neutral, with 2 eq. of fixed base, $Cy_2\,O_2, 2\,MO$; and acid, with 1 eq. of fixed base and 1 of water $Cy_2\,O_2, \left\{\begin{matrix} HO \\ MO. \end{matrix}\right.$ It also forms salts with 1 eq. of two different bases, of which one is always easily reducible, as oxide of silver, mercury and copper, while the other may be difficult to reduce, such as baryta, potash, &c.

The fulminates of silver and mercury, $Cy_2\,O_2, 2\,AgO$, and $Cy_2\,O_2, 2\,HgO$, are examples of the first class. The acid fulminate of zinc $Cy_2\,O_2 \left\{\begin{matrix} HO \\ ZnO, \end{matrix}\right.$ formerly supposed to be fulminic acid, is an example of the second; and the double fulminates of copper and silver, and of potash and silver, $Cy_2O_2\left\{\begin{matrix}CuO\\AgO\end{matrix}\right.$, and $Cy_2O_2\left\{\begin{matrix}KO\\AgO\end{matrix}\right.$ are examples of the third. No neutral fulminates exist with 2 eq. of a difficultly reducible oxide, such as potash, soda, baryta, &c.; nor do any acid fulminates occur with such bases. These very remarkable facts evidently point to some relation, not yet understood, between the oxygen of the base in a salt and the acid of that salt. Of course all the above formulæ may be written according to the theory of compound radicals and hydrogen acids.

To prepare the fulminate of mercury, which is much used for percussion caps, 1 part of mercury is dissolved in 12 parts of nitric acid, Sp. G. 1.36; 11 parts of alcohol at 80 per cent. are added, and the whole is warmed. A brisk reaction soon ensues, very thick white vapours are given off, and the salt is deposited in crystalline grains, mixed with a little metallic mercury. This salt explodes by friction, by percussion, or by heat, and it is a dangerous product, exploding occasionally without apparent cause. An explosion of this nature, not long since, destroyed the distinguished chemist, Mr. Hennell, who was preparing a large quantity in the open air. The fulminate of silver is prepared in the same way, only with 10 parts of nitric acid and 20 of alcohol. Caustic alkalies precipitate from its solution half the silver, forming double fulminates; and chlorides also only precipitate half the silver. Nitric acid, added to the solution, causes a deposit of acid fulminate of silver,

$$Cy_2O_2\left\{\begin{matrix}H\;O\\AgO\end{matrix}\right. \quad \text{or} \quad Cy_2O_4\left\{\begin{matrix}H\\Ag\end{matrix}\right.$$

Hydrochloric acid added to fulminate of silver, gives rise to water, chloride of silver, hydrocyanic acid, and a new acid, chlorohydrocyanic acid C_2NCl_5, H_2. Thus—

$$C_4N_2O_2, 2\,AgO + 7\,HCl = 4\,HO + 2\,AgCl + C_2NH + C_2NCl_5, H_2.$$

3. Cyanuric Acid. $Cy_3O_3, 3\,HO = Cy_3O_6, H_3 = 126{\cdot}75$.

A tribasic acid discovered among the products of the distillation of uric acid. It is formed when solid chloride of cyanogen Cy_3Cl_3 acts on water: $Cy_3Cl_3 + 6\,HO = 3\,HCl + Cy_3O_6, H_3$. It is also formed when urea is heated so as to expel its ammonia. According to what has been stated of the composition of urea, it ought to yield cyanic acid when deprived of its ammonia; but at that temperature 3 eq. of cyanic acid, $3\,CyO, HO$, coalesce to form 1 eq. of cyanuric acid, $Cy_3O_3, 3\,HO$. When, again, acetic acid is added to cyanate of potash, in quantity insufficient to decompose the whole, there is deposited a salt which is an acid cyanurate of potash, $Cy_3O_3 \left\{\begin{matrix} KO \\ 2\,HO. \end{matrix}\right.$

Finally, cyanuric acid is obtained by dissolving melame, ammeline, ammelide and melamine (see those substances) in sulphuric acid, and diluting and heating the solution, until it yields no precipitate with ammonia. On evaporation and cooling, the acid forms prismatic crystals, which are $Cy_3O_3, 3\,HO + 4\,aq$. When dissolved in hot nitric or hydrochloric acid, it is deposited, on cooling, in anhydrous octahedrons. When it has been prepared by heating urea, it is purified by dissolving it in oil of vitriol, and adding nitric acid, drop by drop, till the colour is entirely destroyed. An equal bulk of water is then added, and on cooling, pure cyanuric acid is obtained in crystals.

Cyanuric acid has a weak acid taste, and is sparingly soluble in cold water, more soluble in hot water. Unlike cyanic and fulminic acids, it is very permanent in the uncombined state. When heated in close vessels, it is entirely volatilised in the form of cyanic acid, of which 3 eq. are exactly equal to 1 eq. of cyanuric acid.

As cyanuric acid is formed when urea (cyanate of ammonia) is decomposed by heat, and when cyanate of potass is acted on by acetic acid, and as cyanuric acid, when heated, is resolved into cyanic acid, we have every reason to think that in the former cases, 3 eqs. of cyanic acid coalesce to form one of cyanuric acid; and that, in the latter case, 1 eq. of cyanuric acid is broken up into 3 eqs. of cyanic acid. $3\,(Cy\,O, H\,O) = Cy_3\,O_3, 3\,H\,O$.

Like other tribasic acids, cyanuric acid forms three series of salts, according to the formulæ :—

Hydrated Acid.	Salt with 1 eq. of fixed base.	Salt with 2 eq. of fixed base.	Salt with 3 eq. of fixed base.
$Cy_3O_3, 3\,HO$	$Cy_3O_3 \left\{\begin{matrix} MO \\ 2\,HO \end{matrix}\right.$	$Cy_3O_3 \left\{\begin{matrix} 2\,MO \\ HO \end{matrix}\right.$	$Cy_3O_3, 3\,MO$.

The salts with 1 and 2 eqs. of fixed base are acid; that with 3 eqs. is neutral. With potash and other similar oxides, only the two acid salts are known: with oxide of silver, the salts with 2 and 3 eqs. of oxide.

The three following salts, namely,

Cyanate of Silver.	Fulminate of Silver.	Cyanurate of Silver.
CyO, AgO;	$Cy_2O_2, 2\,AgO$;	$Cy_3O_3, 3\,AgO$

have exactly the same composition in 100 parts; and yet they are in properties entirely dissimilar; this can only be accounted for by some such difference in their formulæ, as is exhibited above. The acids of these salts are all mutually convertible: for when fulminate of silver is decomposed by a salt of ammonia, the fulminate of ammonia is transformed, like the cyanate, into urea; urea when heated yields cyanuric acid; and cyanuric acid when distilled is transformed into cyanic acid. All these circumstances favour the belief that all three are compounds of cyanogen, and that they differ in the absolute number of equivalents of their elements.

Cyamelide; C_2O_2+NH ?

But this is not the end of these transformations: for when cyanic acid is left to itself it becomes turbid and hot, and is soon converted with great heat, into an opaque white solid body, cyamelide, which has no acid properties; and which is also obtained as a white insoluble powder, when fused cyanate of potash is triturated with dried oxalic acid, in which case oxalate of potash is formed, and the cyanic acid, at the moment of being set free, is transformed into cyamelide. Cyamelide is neutral and insoluble in water and acids. It dissolves in aqua potassæ, ammonia being evolved, and the solution yields cyanurate of potash. Heated by itself it yields cyanic acid, which again passes into cyamelide; and when heated with strong sulphuric acid it forms sulphate of ammonia, while carbonic acid escapes: this action is identical with that which occurs when cyanic acid is acted on by water and by acids. All these observations prove that cyamelide is another isomeric modification of cyanic, fulminic, or cyanuric acid. Its probable formula is $C_2\,O_2 + N\,H$, and this, with 2 eqs. HO, yields bicarbonate of ammonia, just as cyanic acid, the formula of which is the same, does. The action of potash is probably this. $4\,(C_2\,O_2\,N\,H) + 3\,H\,O + 4\,K\,O = C_6\,N_3\,O_6, \left\{ \begin{matrix} 2\,K\,O \\ H\,O \end{matrix} \right. + 2\,K\,O, C\,O_2 + N\,H_3$; that is: 4 eqs. cyamelide, 3 eqs. water, and 4 eqs. potash, yield 1 eq. cyanurate of potash, 2 eqs. carbonate of potash, and 1 eq. ammonia.

The three oxygen acids of cyanogen may be fitly compared with the three phosphoric acids; and as we have hitherto made use of the older view of these acids, that which makes them hydrated oxygen acid, we shall, in this comparison, adopt the other theory, and speak of them as hydrogen acids.

	Monobasic.	Bibasic.	Tribasic.
Acids of Cyanogen . .	$Cy\,O_2+H$	$Cy_2\,O_4+H_2$	$Cy_3\,O_6+H_3$
Acids of Phosphorus .	$P_2\,O_6+H$	$P_2\,O_7+H_2$	$P_2\,O_8+H_3$

In the cyanic acids, both the radical and the replaceable hydrogen being doubled and trebled, the capacity of saturation increases in the same ratio. In the phosphoric acids, the capacity of saturation also increases with the replaceable hydrogen, but a great addition to the radical has no corresponding effect in increasing either the replaceable hydrogen or the neutralising power. Thus, if to tribasic phosphoric acid $P_2 O_8 + H_3$ we add 2 eqs. of $P_2O_5 = P_4O_{10}$ we obtain $P_6 O_{18} + H_3 = 3(P_2 O_6 + H)$; that is, the acid becomes monobasic, but the quantity of base neutralised is the same after that addition as before. Notwithstanding this difference, however, the analogy between the monobasic, bibasic, and tribasic acids of cyanogen and phosphorus, as well as that between their salts, is most interesting and worthy of attention. As we believe that the phosphoric acids contain three different radicals, $P_2 O_6$, $P_2 O_7$, and $P_2 O_8$, so we may admit that the three cyanic acids have each a distinct radical; only in this case the three radicals are alike in composition, and differ in their relative weight: the first being $C_2 N = Cy$; the second $C_4 N_2 = Cy_2$; and the third $C_6 N_3 = Cy_3$; or, in other words, these radicals are three different cyanogens. The relations of chlorine to cyanogen countenance this idea.

CYANOGEN AND NITROGEN.

Mellone $= Cy_3 N = C_6 N_4 = Me = 93$.

Cyanogen, when it combines with nitrogen in the proportion of 3 eq. Cy to 1 eq. $N = C_6 N_4$, produces a very remarkable compound, discovered by Liebig, and called mellone, which being itself a well marked compound radical, will be described as such, and not as a compound of cyanogen and nitrogen.

CYANOGEN AND CHLORINE.

Cyanogen forms two chlorides: one gaseous, but compressible, obtained by the action of chlorine gas on dry hydrocyanic acid; the other solid, formed by a spontaneous transformation of the former when kept in the liquid form in sealed tubes. Both are volatile and both contain cyanogen and chlorine, equivalent for equivalent. But the vapour of the solid chloride is three times denser than that of the other; and, moreover, the solid chloride, in contact with water, produces hydrochloric and cyanuric acids: while the gaseous chloride, under the same circumstances, gives rise to hydrochloric acid, and cyanic acid, the latter with water, at once passing into bicarbonate of ammonia, so that the final result is sal ammoniac and carbonic acid.

These considerations prove that the two chlorides are isomeric: that the first or gaseous chloride is Cy Cl; and that the solid chloride is $Cy_3 Cl_3$, and is formed by the junction of 3 eq. of the other; and we are consequently justified in extending this view to cyanic and cyanuric acids, and in supposing the vapour of the latter to be three times more condensed than the vapour of cyanic acid: and the cyanogen of cyanuric acid to be the cyanogen of the solid chloride, and three times denser than ordinary cyanogen.

CYANOGEN WITH BROMINE AND IODINE.

With these elements cyanogen readily combines when cyanide of mercury is distilled with bromine or iodine. The bromide and iodide are both volatile, and crystallisable, pungent and poisonous.

To judge by the density of their vapours, these compounds are $Cy\,Br$ and $Cy\,I$, corresponding to the liquid chloride, which is also very pungent and irritating to the eyes.

CYANOGEN AND SULPHUR.

Bisulphuret of Cyanogen. $Cy\,S_2 = 58{\cdot}5$.

When sulphocyanide of potassium, (see that salt) is acted on by chlorine or by dilute nitric acid, there is obtained an orange-yellow powder, which contains sulphur and cyanogen, and which is supposed by some to be bisulphuret of cyanogen, by others to contain hydrogen. This question will be considered hereafter, for whether this be so or not, there is a compound, possibly that compound, of sulphur and cyanogen, which acts as a radical, and is hence called sulphocyanogen. It will be described separately, since it is far more important as a radical than as a compound of cyanogen.

CYANOGEN AND METALS.

With metals, cyanogen forms compounds which in many cases are analogous to the chlorides of the same metal. When the metal is easily reducible, such as silver, mercury or palladium, the cyanide is formed by the action of hydrocyanic acid on the oxide, or its salts: $MO + H\,Cy = HO + M\,Cy$. In the case of difficultly reducible metals, such as potassium, hydrocyanic acid seems to combine with the oxide, not being able to reduce it, until another cyanide is added, which tends to form a double cyanide.

Cyanide of Potassium, $= K\,Cy$ is best formed by heating to whiteness in close vessels the ferrocyanide of potassium, a salt which may be viewed as containing cyanide of iron and cyanide of potassium. The former is converted into insoluble carburet of iron; the latter remains unchanged, and may be mechanically picked out, or dissolved by hot alcohol of 60 p. c., which deposits it on cooling. Or, an alcoholic solution of pure and dry hydrocyanic acid is added to an alcoholic solution of potash; or, lastly, the vapours of hydrocyanic acid, formed on the process given at p. 284, are conducted into an alcoholic solution of potash, kept cool, when the salt is deposited.

It is white, and crystallisable in cubes. It has no smell when pure, but when exposed to moist air, smells of hydrocyanic acid. It is very poisonous. When heated it fuses easily, and is not altered by heat in close vessels. Heated in the air it absorbs oxygen and is converted into cyanate of potash $KCy+O_2=KO.Cy\,O$. It is very soluble and deliquescent, and its solution, attracting carbonic acid from the air, gives off hydrocyanic acid: hence its smell.

Cyanide of Sodium is analogous to the preceding salt.

Cyanide of Zinc, $Zn\,Cy$ is obtained by adding hydrocyanic acid to acetate of zinc. It is a snow-white insoluble powder, which is used in medicine.

Cyanide of Iron.—Protocyanide of iron, $Fe\,Cy$, has not been isolated. There appears to exist a percyanide, also not yet isolated, $Fe_2\,Cy_3$; and, according to Pelouze, there may be obtained an intermediate cyanide, $Fe_3\,Cy_4$, analogous to the magnetic oxide of iron, as a green powder.

But although the cyanides of iron are little known, there are some very important compounds, especially those of two radicals, which contain those elements, namely, cyanogen and iron, along with hydrogen, and with metals. These will be described after we have gone over the simple cyanides of the metals.

Cyanide of Cobalt, $Co\,Cy$, is obtained as a brownish-white precipitate, by adding hydrocyanic acid to the acetate of cobalt. Cobalt also forms compounds analogous to those of iron above alluded to, with cyanogen, &c.

Bicyanide of Mercury, $Hg\,Cy_2$, is easily obtained by dissolving red oxide of mercury in very dilute hydrocyanic acid, till the smell of the acid is destroyed. The liquid, rendered neutral, if necessary, by a few drops of hydrocyanic acid, yields fine crystals, on evaporation and cooling. Or it may be made by the action of three parts of persulphate of mercury on two of ferrocyanide of potassium dissolved in fifteen of hot water, which is boiled and filtered, and the filtered liquid on cooling deposits the bicyanide.

It forms regular prismatic crystals, permanent in the air, of a horrible metallic taste, soluble in water and alcohol. It is used for making cyanogen, also to prepare hydrocyanic acid by one process, and to yield the bromide and iodide of cyanogen.

Cyanide of Silver. $Ag\,Cy$.—Formed by the action of hydrocyanic acid or cyanide of potassium on nitrate of silver. It is exactly similar to the chloride, white, curdy, insoluble in water or acids, soluble in ammonia. It is decomposed by hydrochloric acid, yielding hydrocyanic acid.

Cyanide of Palladium, $\mathrm{Pd\,Cy}$.—The affinity of cyanogen for palladium is most powerful, and hydrocyanic acid, or a soluble cyanide, when added to a salt of oxide of palladium, precipitate the cyanide as a grey powder. This property serves for separating palladium from other metals.

Cyanides of Gold.—The protocyanide, $\mathrm{Au\,Cy}$, is formed by adding cyanide of potassium in excess to protochloride of gold, till a clear solution is formed, and then adding hydrochloric acid, which precipitates the protocyanide as a bright-yellow powder, very permanent, and soluble in cyanide of potassium.

The tercyanide, $\mathrm{An\,Cy_3}$, is formed by the action of cyanide of potassium on terchloride of gold, and appears as whitish-yellow precipitate, soluble in cyanide of potassium, insoluble in acids.

DOUBLE CYANIDES OF THE METALS.

The insoluble metallic cyanides, such as those of iron, cobalt, copper, silver, gold, platinum, and others, dissolve readily in cyanide of potassium, or sodium, forming crystallisable double cyanides, which are not affected by soluble carbonates nor by chlorides, but are generally decomposed by acids, which precipitate the insoluble cyanide. If these double cyanides, which may be $2\,\mathrm{K\,Cy} + \mathrm{m\,Cy}$ (m Cy being an insoluble metallic cyanide) are added to the solution of the oxide of another metal forming also an insoluble cyanide, this latter metal takes the place of the potassium, and a new double insoluble cyanide is the result. Thus $(2\,\mathrm{K\,Cy} + \mathrm{m\,Cy}) + 2\,\mathrm{MO} = 2\,\mathrm{KO} + (2\,\mathrm{M\,Cy} + \mathrm{m\,Cy})$. (Here m may be iron and M copper or lead.) Now, as these double cyanides, thus precipitated, are of various and often characteristic colours, the ferrocyanide of potassium, $2\,\mathrm{K\,Cy} + \mathrm{Fe\,Cy}$, is extensively used as a test for metals.

The protocyanide of iron, the percyanide of iron, the percyanide of cobalt, and perhaps some others, not only form double salts with the elements of cyanide of potassium, but also produce very remarkable acids, by combining with the elements of hydrocyanic acid, that is, with hydrogen replacing the potassium of the double salt. Thus ferrocyanic acid is $2\,\mathrm{H\,Cy} + \mathrm{Fe\,Cy}$, and so on. In these compounds the hydrocyanic acid is no longer poisonous, and it is therefore highly probable that these acids, and their corresponding salts, really contain new and very peculiar radicals. The assumption of these radicals will alone enable us to classify or remember these compounds.

IV. FERROCYANOGEN. $Cy_3\ Fe = Cfy = 105{\cdot}87$.

We assume, then, the existence of this radical as the basis of ferrocyanide of potassium, or prussiate of potash. It is bibasic, combining with 2 eq. of hydrogen or of metals. The following formulæ expresses the composition of ferrocyanic acid, and of ferrocyanide of potassium, &c.

Ferrocyanic Acid $= Cfy, H_2 = Cy_3\ Fe, H_2 = 2\ H\ Cy + Fe\ Cy$.
Ferrocyanide of Potassium $= Cfy, K_2 = Cy_3\ Fe, K_2 = 2\ K\ Cy + Fe\ Cy$.
——— Iron $= 3 Cfy, Fe_4 = 3 Cy_3\ Fe, Fe_4 = 9\ Cy + 7\ Fe$.

It will be seen, by the two first compounds, that we may consider them either as compounds of the radical Cfy with hydrogen or metals, or as double cyanides. In the third, which is the formulæ of Prussian blue, we see that the iron exists in two different states, in one of which it cannot be detected by the usual tests. That form is the radical Cfy, which exists also in the two preceding compounds.

Ferrocyanic Acid. $Cfy, H_2 = 107{\cdot}87$.

This very interesting compound is obtained by mixing a cold saturated solution of ferrocyanide of potassium with one quarter its volume of strong hydrochloric acid, and, agitating the mixture with half its bulk of pure ether, the ether rises to the surface, carrying with it, suspended, a white crystalline substance, which when washed with ether and dried, is ferrocyanic acid. It is soluble in water and alcohol, has a decidedly acid taste and reaction, and decomposes the alkaline carbonates, forming, with carbonate of potash, the ferrocyanide of potassium. The production of this compound by the action of hydrochloric acid on ferrocyanide of potassium is very easily explained. $Cfy, K_2 + 2\ H\ Cl = Cfy, H_2 + 2\ K\ Cl$.

Although this compound may be represented as a combination of cyanide of iron with hydrocyanic acid, $Fe\ Cy + 2\ H\ Cy$, there is every reason to believe that it contains no hydrocyanic acid, as such. For not only is it far more strongly acid, (and protocyanide of iron cannot be supposed to give acid properties to hydrocyanic acid,) but it is totally destitute of all poisonous properties, for both it and its salts may be taken internally without further effect than the laxative action common to most neutral salts.

Ferrocyanic acid, being bibasic, forms two kinds of salts: in the first the 2 eq. of hydrogen are replaced by 2 eq. of potassium, sodium, &c.; &c., in the second, they are replaced by equivalents of two different metals: such as potassium and barium. An example of the first class is, $Cfy + K_2$; of the second,

$\mathrm{Cfy}\left\{\begin{matrix}\mathrm{K}\\ \mathrm{Ba}\end{matrix}\right.$. Of all these compounds, by far the most important is the ferrocyanide of potassium, or prussiate of potash, from which all the compounds of cyanogen may be prepared, and which is manufactured on the large scale, being also used in the arts.

Ferrocyanide of Potassium. SYN. Prussiate of Potash. Anhydrous, $\mathrm{Cfy\,K_2}$, 184·17. Crystallised, it is $\mathrm{Cfy,K_2 + 3\,HO} = 211{\cdot}2$. —This valuable salt is prepared by fusing animal matter, such as dried blood, hoofs, hair, horns, &c., or the animal charcoal remaining after such matters have been distilled to obtain carbonate of ammonia, with potashes or pearlash, in iron vessels, as long as gas is disengaged. The melted mass is then withdrawn from the fire, and when cold, lixiviated with water, the solution digested with the insoluble part, filtered and evaporated, when it deposits, on cooling, yellow crystals; which by a second solution and crystallisation become quite pure.

The essential points of this process are, first, the presence of as much nitrogen as possible in the animal matter: hence fresh, dried, uncalcined animal matter is far preferable to animal charcoal: secondly, the presence of metallic iron or sulphuret of iron: the former is either directly derived from the vessels, which are rapidly corroded, or added as filings; the latter is formed from the iron of the vessels by the action of bisulphuret of potassium, which arises from the decomposition, by charcoal at a red heat, of the sulphate of potash contained in the potashes or pearlash; hence pure carbonate of potash is not adapted to this process. Thirdly, the exclusion of the air as far as possible, in order to prevent the oxidation and destruction of the cyanide of potassium formed.

The explanation of the process is very simple and beautiful, and we are indebted for it to the researches of Liebig. When animal matter is heated along with potash, cyanogen is formed, and combining with the potassium (set free at the same time by the action of carbon on potash) produces cyanide of potassium, a salt which is not decomposed by a red heat in closed vessels. At the same time, metallic iron and sulphuret of iron are present in the mixture, but not a trace of the ferrocyanide, previous to the action of water, for the very obvious reason, that the ferrocyanide is decomposed by a red heat, into cyanide of potassium and carburet of iron, nitrogen being disengaged.

If the cooled mass be now digested in water, the cyanide of potassium dissolves, either the metallic iron with disengagement of hydrogen, or the sulphuret of iron, and the filtered liquid now contains the ferrocyanide.

Direct experiments have shown that cyanide of potassium dissolves either iron, oxide of iron, or sulphuret of iron, producing the ferrocyanide; $3\,K\,Cy + Fe + H\,O = (2\,K\,Cy + Fe\,Cy) + K\,O + H$. Or, $3\,K\,Cy + Fe\,S = (2\,K\,Cy + Fe\,Cy) + K\,S$. And it has also been shown by Liebig that if the fused mass be lixiviated with alcohol, the residue, when treated with water, yields no ferrocyanide, while the alcohol contains none, but only cyanide of potassium.

Taking these facts into consideration, perhaps the best method would be to use pure carbonate of potash, free from sulphate, by which means no sulphuret of potassium would be formed, and the iron vessels would not suffer as they now do. The cyanide of potassium, being dissolved in water and filtered, should then be placed in contact with iron turnings in flat open vessels, when, the third part of the potassium being oxidised by the air, the iron is rapidly dissolved, and a quantity of ferrocyanide obtained equal to that indicated by the cyanide of potassium present.

The ferrocyanide of potassium forms large honey-yellow, transparent, flat, quadrangular prisms, derived from a rhombic octahedron. It is very soluble in water, and forms precipitates in almost all metallic solutions, many of which are characteristic. Thus, with solutions of zinc and lead, it gives a white precipitate, with those of copper a chesnut brown, with those of peroxide of iron a deep blue, with protoxide of iron a pale blue, with those of barium and calcium whitish-yellow crystalline precipitates. The lead precipitate is Cfy, Pb_2; that of copper Cfy, Cu_2; those of barium and calcium $Cfy \left\{ \begin{matrix} K \\ Ba \end{matrix} \right.$ and $Cfy \left\{ \begin{matrix} K \\ Ca \end{matrix} \right.$; and that of zinc, $2\,Cfy + \left\{ \begin{matrix} Zn_3 \\ K \end{matrix} \right. + 6\,aq = Cfy, Zn_2 + Cfy \left\{ \begin{matrix} Zn \\ K \end{matrix} \right. + 6\,aq$. That of protoxide of iron is $2\,Cfy \left\{ \begin{matrix} Fe_3 \\ K \end{matrix} \right. = Cfy, Fe_2 + Cfy \left\{ \begin{matrix} Fe \\ K \end{matrix} \right.$. All of these formulæ are easily referred to the general formula of the ferrocyanides, Cfy, M_2.

Ferrocyanide of Iron.—But the most remarkable of all these compounds is that formed with persalts of iron, namely Prussian blue. It is produced when ferrocyanide of potassium comes in contact with perchloride, or any salt of peroxide of iron. Now as ferrocyanogen is a bibasic radical, 1 eq. of it corresponds to 2 eq. of potassium, hydrogen, oxygen, chlorine, &c.; and as perchloride of iron, $Fe_2\,Cl_3$, contains 3 eq. of chlorine, $1\frac{1}{2}$ eq. of ferrocyanide of potassium will be required to decompose 1 eq. of it, or, to avoid fractions, 3 eq. of ferrocyanide $Cfy_3\,K_6 = 3\,Cfy, K_2$, are required for 2 eq. perchloride of iron, $Fe_4\,Cl_6 = 2\,Fe_2\,Cl_3$. The result is, $Cfy_3\,K_6 + Fe_4\,Cl_6 = 6\,K\,Cl + Cfy_3\,Fe_4$; and this last is the true formula of Prussian blue, although, from its tendency to combine both with ferrocyanide of potassium and with oxide of iron, its analysis offers great difficulties. The formula $Cfy_3\,Fe_4$ or $Fe_4\,Cfy_3$ shows that Prussian blue corresponds to peroxide and perchloride (sesquioxide and sesquichloride) of iron, $Fe_2\,O_3$ and $Fe_2\,Cl_3$, for Cfy being bibasic is equivalent to Cl_2 or O_2, and consequently $Fe_4\,Cy_3$ is equivalent to $Fe_4\,Cl_6$ or $Fe_4\,O_6$, that is, to $2\,Fe_2\,Cl_3$ and $2\,Fe_2\,O_3$. It must be admitted to be a very strong argument in favour of the existence of ferrocyanogen, as a bibasic radical, according to the theory of Liebig, that Prussian blue, on all other theories the most complex and anomalous compound in the whole range of chemistry, becomes quite normal and one of a series.

Ferrocyanide of potassium is employed to yield cyanogen and all its compounds. We have already seen how cyanogen, hydrocyanic acid, cyanide of potassium, cyanate of potash, urea, cyanic and cyanuric acids, and ferrocyanic acid are obtained from it. Cyanide of potassium, for testing, and to be used as a flux and in analysis, is best prepared, according to Liebig, by heating 8 parts of the dry ferrocyanide with 3 of pure carbonate of potash in an iron vessel till the fused mass is colourless. It is then poured off from the sponge of reduced iron, and kept in well-stoppered bottles. This very useful preparation, known as Liebig's cyanide of potassium, is not quite pure, containing a little cyanute of potash: but this does not interfere with its use. But another very remarkable compound is produced by the action of a current of chlorine gas on the solution of ferrocyanide, if transmitted until the solution ceases to produce Prussian blue with perchloride of iron, yielding only a brownish-green colour, but no precipitate. The liquid now gives, on evaporation, beautiful deep hyacinth red crystals of a new salt, the ferridcyanide of potassium, discovered by Gmelin. This salt contains a new radical, ferridcyanogen.

V. FERRIDCYANOGEN. $Cy_6\,Fe_2 = Cfdy = 211{\cdot}74$.

This radical has not yet been isolated. It is formed by the coalescence of 2 eq. of ferrocyanogen, and is tribasic. It forms an acid with hydrogen, and salts with metals.

Ferridcyanic Acid. $(2\,Cfy + H_3) = Cfdy, H_3 = 214{\cdot}74$.

This acid is obtained from the lead salt $Cfdy, Pb_3$, by the action of sulphuric acid. It is soluble in water, and by the action of sulphuretted hydrogen, is converted into ferrocyanic acid: $2\,Cfy, H_3 + H\,S = 2\,(Cfy, H_2) + S$. With bases it forms salts; as with potash the ferridcyanide of potassium.

Ferridcyanide of potassium. Syn. Red prussiate of potash. Its preparation has been described above. Its formula is $2\,\mathrm{Cfy} + \mathrm{K}_3 = \mathrm{Cfdy}, \mathrm{K}_3$; and it is quite anhydrous. Like the yellow prussiate, it forms precipitates with most metallic solutions, many of which are characteristic. With salts of peroxide or with perchloride of iron, it only strikes a brown or green colour, but with protochloride or salts of protoxide, it forms prussian blue. As the radical is tribasic, 1 eq. of it ought to be equivalent to 3 eq. of oxygen, chlorine, &c., and if we suppose the potassium in the ferridcyanide replaced by its equivalent of iron, we should have $\mathrm{Cfdy}, \mathrm{Fe}_3 = \mathrm{Fe}_5\,\mathrm{Cy}_6$; for $\mathrm{K}_3\,\mathrm{Cfy}_2 + 3\,\mathrm{Fe\,O} = \mathrm{Fe}_3\,\mathrm{Cfy}_2 + 3\,\mathrm{KO}$; and $\mathrm{Fe}_3\,\mathrm{Cfy}_2 = \mathrm{Fe}_5\,\mathrm{Cy}_6$. But, instead of this compound, there is formed prussian blue, the same we have above described as being formed by the action of yellow prussiate or peroxide of iron. In fact, when the red prussiate is added to a solution of a salt of protoxide, or to protochloride of iron, yellow prussiate is formed along with prussian blue and a salt of potash. Bearing in mind, as in all the above explanations, that 1 eq. ferridcyanogen Cfdy is equal to 2 eq. ferrocyanogen Cfy, and that, consequently, the red prussiate, $\mathrm{Cfdy}, \mathrm{K}_3$ may be equally well represented as $2\,\mathrm{Cfy}, \mathrm{K}_3$, then we have $2\,(2\,\mathrm{Cfy}, \mathrm{K}_3) + 4\,(\mathrm{Fe\,O}, \mathrm{SO}_3) = (3\,\mathrm{Cfy} + \mathrm{Fe}_4) + (\mathrm{Cfy}, \mathrm{K}_2) + 4\,(\mathrm{K\,O}, \mathrm{S\,O}_3)$.

The ferridcyanide of potassium may be viewed as ferrocyanide of potassium, *plus* a certain amount of ferrocyanogen; $2\,(\mathrm{Cfdy}, \mathrm{K}_3) = 3\,(\mathrm{Cfy}, \mathrm{K}_2) + \mathrm{Cfy}$.

With salts of lead, ferridcyanide of potassium forms the ferridcyanide of lead, $\mathrm{Cfdy}, \mathrm{Pb}_3$.

VI. Cobaltocyanogen. $\mathrm{Cy}_6\,\mathrm{Co}_2 = \mathrm{Cky} = 216{\cdot}52$.

Not yet isolated, but known in combination with hydrogen; potassium, &c. It is analogous to ferridcyanogen in constitution, and like it, is tribasic.

Cobaltocyanic acid $\mathrm{Cky\,H}_3 = 219{\cdot}52$.—Obtained by the action of sulphuric acid on cobaltocyanide of lead $\mathrm{Cky}, \mathrm{Pb}_3$. It forms silky filaments, which are deliquescent and strongly acid.

Cobaltocyanide of Potassium, Cky, K.—Is obtained by acting on a salt of oxide of cobalt with solution of cyanide of potassium and hydrocyanic acid, when hydrogen is given off and the new salt is obtained in crystals. The protocyanide of cobalt, precipitated on the first addition of cyanide of potassium, redissolves in an excess of that salt, forming a compound, $2\,\mathrm{Co\,Cy} + \mathrm{K\,Cy}$, or $2\,\mathrm{Co\,Cy} + 3\,\mathrm{K\,Cy}$. At all events there is enough of cyanide of potassium present to form the latter compound. The hydrocyanic acid, being now added, yields 1 eq. of cyanogen, converting the 2 eq. of protocyanide into 1 eq. of sesquicyanide of cobalt, while hydrogen is given off: $2\,Co\,Cy + H\,Cy = Co_2\,Cy_3 + H$. Lastly, the sesquicyanide $Co_2\,Cy_3$, with the 3 eq. of cyanide of potassium, $3\,K\,Cy$, produces the cobaltocyanide of potassium, $Cy_6\,Co_2 + K_3 = Cky, K_3$. The crystals are isomorphous with those of the red prussiate of potash; they are yellow, soluble; their solution is not altered by acids, and gives, in solutions of protoxide of cobalt, a beautiful rose-coloured precipitate, analogous probably to prussian blue; possibly, however, it may be Cky, Co_3. It precipitates many other metallic solutions, such as those of lead and silver.

Cobaltocyanide of potassium is a singularly permanent salt, resisting the action of the strongest acids; which is, in itself, a sufficient proof that it cannot contain cyanide of potassium as such. With the salts of nickel it forms a green precipitate, Cky, Ni_3, which is insoluble in boiling dilute acids. This property has been applied by Liebig to the separation of cobalt from nickel in analysis. All other metals being removed, an excess of potash is first added, and then hydrocyanic acid till the precipitate at first formed is dissolved, and the whole is then boiled. Hydrochloric acid is now added, and if no nickel be present, it produces no change, because it has no action on cobaltocyanide of potassium. But if nickel be present (of course by this time as cyanide) it is converted into chloride, and this is instantly precipitated by the cobaltocyanide of potassium as cobaltocyanide of nickel. Should there be more cobalt than nickel present, the whole nickel is precipitated, and the precipitate, acted on by potash, leaves the nickel as peroxide, while the cobalt is dissolved as cobaltocyanide, and may be determined along with the portion not precipitated for want of nickel. If, on the other hand, there be more nickel than cobalt, all the cobalt is contained in the green precipitate of cobaltocyanide of nickel, and may be dissolved by potash, and its quantity determined, while the nickel left by the potash as peroxide may be added to that left in the liquid for want of cobalt. Such is an outline of this very beautiful and refined method, which gives most accurate results.

VII. Chromocyanogen. $Cy_6\,Cr_2 = Cry$.

This radical is little known. It is analogous to the two preceding, forming with hydrogen an acid, Cry, H_3, and with potassium a yellow crystallisable salt, Cry, K_3, which precipitates metallic solutions.

VIII. PLATINOCYANOGEN. $Pt\,Cy_2 = Cpy = 151{\cdot}38$.

This radical is not known in the separate state. It forms with hydrogen a crystallisable acid of a gold or copper colour and metallic lustre, Cpy, H_2, which is very soluble and deliquescent. This acid is powerful, decomposes the carbonates, and produces platinocyanides. Platinocyanide of potassium, Cpy, K_2, is obtained by heating spongy platinum to low redness with dried ferrocyanide of potassium, and lixiviating with water; or by dissolving protochloride of platinum in hot solution of cyanide of potassium. It forms crystals yellow and metallic by transmitted, blue by reflected light. By the action of this salt on protonitrate of mercury, a cobalt-blue precipitate is formed, which, when heated in the fluid, becomes white, and is then pure platinocyanide of mercury, Cpy, Hg (?) This salt, acted on by sulphuretted hydrogen, yields the platinocyanic acid. A solution of platinocyanide of potassium acted on by chlorine, yields beautiful copper-like crystals of a new salt, which is either a double cyanide, $2\,K\,Cy + Pt_2\,Cy_3 + 5\,HO$; or the potassium salt of a new radical, $Pt_2\,Cy_5, K_2 + 5\,HO$. (Knop.)

The platinocyanides of barium, strontium, and calcium, are easily obtained by the action of platinocyanic acid on these bases, and crystallise readily in beautiful greenish yellow colour, or in some cases green and red with metallic lustre.

IX. IRIDIOCYANOGEN. $Cy_3\,Ir = Ciy$.

This radical has not been isolated—it forms, with hydrogen, iridiocyanic acid $Cy_3\,Ir, H_2$, which is obtained by the action of sulphuretted hydrogen on iridiocyanide of lead $Cy_3\,Ir, Pb_3$.

Iridiocyanide of Potassium, $Cy_3\,Ir, K_2$, is obtained by the action of protochloride of irridium on cyanide of potassium. It forms colourless crystals; its solution gives, with salts of peroxide of iron, a deep indigo colour.

There appears to be a series of similar compounds formed by cyanide of palladium. The palladiocyanide of potassium corresponds to the platinocyanide, and its formula is $Cy_2\,Pd, K$.

There is also reason to believe that manganese forms a manganocyanogen, corresponding to ferridyanogen, $Cy_6\,Mn_2 = Cmy$. The manganocyanide of potassium is probably $Cy_6\,Mn_2 + K_3 = Cmy, K_3$.

From what has been stated in the preceding pages, it will be seen that cyanogen has a very great tendency to form cyanides containing 2 or 3 metals, and likewise cyanides containing one of these metals and hydrogen in the place of the other. As these latter compounds are very powerful acids, we are naturally led to consider them as hydrogen acids, in which the hydrogen is combined with radicals. This view has been adopted above, and we have seen reason to admit the following radicals :—

Platinocyanogen Cpy $= Cy_2$ Pt
Palladiocyanogen Cpdy $= Cy_2$ Pd
Ferrocyanogen Cfy $= Cy_3$ Fe
Iridiocyanogen Ciy $= Cy_3$ Ir
Ferridcyanogen = Cfdy $= Cy_6 \ Fe_2$
Cobaltocyanogen = Cky $= Cy_6 \ Co_2$
Chromocyanogen = Cry $= Cy_6 \ Cr_2$
Manganocyanogen = Cmy $= Cy_6 \ Mn_2$

It will be observed that there are three different formulæ among these radicals, namely, $Cy_2 M$; Cy_3, M ; and $Cy_6 M_2$; the first monobasic, the second bibasic, the third tribasic. No other view can at present be given of these compounds, of their acids, and of their salts, which is at once so satisfactory, so consistent, and so advantageous for the learner, as being adapted to assist the memory. It is true that the acids may be viewed as compounds of cyanide of a metal with cyanide of hydrogen (hydrocyanic acid), and their salts as compounds of two metallic cyanides. Thus, ferrocyanic acid, $Cy_3 Fe + H_2$, may be said to be 2 HCy + Fe Cy, and ferrocyanide of potassium, 2 KCy + Fe Cy. Again, ferridcyanic acid may be 3 HCy + $Fe_2 Cy_3$ and its potassium salt 3 KCy + $Fe_2 Cy_3$; while platinocyanic acid and its potassium salt may be HCy + PtCy and KCy + Pt Cy.

But the strong acid properties and inert nature of these acids, and the remarkable permanence, both of the acids and of the salts, are entirely inconsistent with the presence of so weak an acid and so frightful a poison as hydrocyanic acid, or of bodies so easily decomposed as hydrocyanic acid and cyanide of potassium. Besides, there are numerous double cyanides, such as K Cy, Zn Cy ; KCy, Cd Cy ; K Cy, Cu_2 Cy, &c. &c. &c., which act as such ; being easily decomposed, and exhibiting no indications of containing radicals like those above described. We shall therefore not dwell on any other view, and merely allude here to the true double cyanides, as belonging more to the history of the metals, and less to that of the organic radicals.

PARACYANOGEN.

As an appendix to the metallic cyanides, we may here mention this compound, which is left behind as a dark-brown powder, when cyanide of mercury is heated in a retort. As cyanogen and mercury alone are given off, we should expect the salt to be dissipated by heat entirely ; but this not being the case, it is evident that the residue, if it contain no mercury, must have the same composition as cyanogen, and be, in short, an isomeric modification of it—a solid cyanogen. Again, when cyanide of silver is heated, it gives off part of its cyanogen ; it then glows, and, if soon removed from the fire, yields a peculiar residue, which is only partly dissolved by nitric acid. The insoluble residue appears to contain silver and cyanogen in the proportion $Ag\,Cy_3$, and it is probable that the cyanogen here is in the solid modification, of which 1 eq. is supposed to be formed by 3 eq. of cyanogen.

Whether, therefore, we admit paracyanogen as a separate radical or not, the two residues just mentioned contain carbon and nitrogen in the proportions to form cyanogen. It is also possible that some such compound may exist in cast iron and steel, which appear to contain nitrogen as well as carbon.

In treating of mellone, we shall see that doubts may be entertained of the existence of paracyanogen, and that the proportions of carbonic acid and nitrogen gases obtained in analysing the supposed paracyanogen may be derived from a mixture of mellone and carbon.

CYANOGEN AND SULPHUR.

X. Sulphocyanogen. $Cy\,S_2 = Csy$.

Syn. *Bisulphuret of Cyanogen.*—When ferrocyanide of potassium is heated with sulphur, there is formed a new salt, the formula of which is $Cy\,S_2 + K$. This is sulphocyanide of potassium, which appears to contain the radical $Cy\,S_2$, or Csy. We cannot say that this radical is known in the free state, but by the action of chlorine on sulphocyanide of potassium there is formed a bright orange powder, which contains sulphocyanogen, mixed with some other bodies. Like the preceding radicals, sulphocyanogen, with hydrogen, forms a peculiar acid, the sulphocyanic or hydrosulphocyanic acid.

Hydrosulphocyanic Acid—$Cy\,S_2, H = Csy\,H$—is obtained by passing sulphuretted hydrogen gas through sulphocyanide of lead, Csy, Pb, suspended in water. The solution thus formed is highly acid, and has the odour of acetic acid. It strikes a blood-red colour with salts of peroxide of iron, and this property is found in all soluble sulphocyanides. The formula of this acid corresponds to that of cyanic acid, $Cy\,O_2, H$; and it may be viewed as cyanic acid, the oxygen of which has been replaced by sulphur. With metallic oxides, it forms the sulphocyanides of the metals ; $Cy\,S_2, H + M\,O = Cy\,S_2, M + HO$.

Sulphocyanide of Potassium—$Cy\,S_2, K = Csy, K$. The best process for obtaining this salt is to melt at a gentle heat (only raised at the end to low redness) 46 parts of dried ferrocyanide of potassium, 32 of sulphur, and 17 of pure carbonate of potash. The mass when cold is boiled with water, and the solution, being filtered and evaporated, deposits striated prismatic crystals of the salt, very similar in appearance, and in taste also, to nitre.

If not quite pure, it is purified by solution in alcohol and recrystallisation. In this process, the whole cyanogen of the ferrocyanide is first converted into cyanide of potassium, and then, by the taking up of sulphur, into sulphocyanide; while the iron is converted into sulphuret. As 1 eq. ferrocyanide contains 3 eq. of cyanogen and 2 of potassium, 1 eq. of carbonate of potash is added, and the 3 eq. of cyanide of potassium thus obtained take up 6 eq. of sulphur to form the new salt. $3\,K\,Cy + S_6 = 3\,(Cy\,S_2, K)$.

Sulphocyanide of potassium causes precipitates in some metallic solutions, but as many metallic sulphocyanides are soluble, the greater number of metals are not precipitated by this salt. With salts of peroxide of iron it strikes an intense blood-red colour, but causes no precipitate. With acetate of lead it gives yellow crystals, and with subacetate a white precipitate, and with salts of suboxide of copper also an insoluble white subsulphocyanide of copper. Sulphocyanide of silver is precipitated as a curdy white solid, when sulphocyanide of potassium is added to nitrate of silver. The other sulphocyanides are soluble.

When sulphocyanic acid is set free from its salts, by diluted acids, and exposed to heat, it is resolved, with the aid of the elements of water, into carbonic acid, bisulphuret of carbon, and ammonia. $C_2NS_2, H + H_2O_2 = \left.\begin{matrix} CS_2 \\ CO_2 \end{matrix}\right\} + N\,H_3$. Compare this with the spontaneous decomposition of cyanic acid when set free from its salts: $C_2NO_2, H + H_2\,O_2 = \left.\begin{matrix} CO_2 \\ CO_2 \end{matrix}\right\} + N\,H_3$. This shows that the view which considers sulphocyanic acid as cyanic acid, the oxygen of which has been replaced by sulphur, is confirmed by the similarity in the decomposition of these two acids; which, in this point of view, may be said to belong to the same type.

When sulphocyanide of potassium is mixed with 6 or 8 volumes of strong hydrochloric acid, hydrocyanic acid is given off, and a new crystalline acid is deposited, which contains more sulphur, and may be called (hydro) persulphocyanic acid. $3\,(Cy\,S_2, H)$, that is 3 eq. of sulphocyanic acid lose Cy H, 1 eq. of hydrocyanic acid, and there remain 2 eq. of the compound $Cy\,S_3$, H, or persulphocyanic acid. The formula of its salts is $Cy\,S_3$, M. When the acid is dissolved in ammonia, it soon deposits sulphur, and the liquid retains a new compound $Cy_2\,S_5, H_2$ (= $2\,Cy\,S_3$, H — S) combined with ammonia: on adding an acid, persulphocyanic is reproduced and deposited, while sulphocyanic acid remains in the solution: $Cy_2S_5, H_2 = \begin{cases} CyS_3, H \\ CyS_2, H \end{cases}$

When solution of sulphocyanide of potassium is acted on by chlorine, or by nitric acid, a bright orange-yellow powder is deposited, which was long supposed to be sulphocyanogen; but it now appears to be a compound or mixture of sulphocyanogen, sulphocyanic acid, and water, in the proportions $3\,Cy\,S_2 + Cy\,S_2, H + HO = C_6\,N_3\,S_6 + (C_2NS_2, H) + HO = C_8N_4S_8H_2O$. This yellow compound undergoes a very remarkable change when heated: it gives off bisulphuret of carbon, sulphur, and a little persulphocyanic acid, and there is left in the retort a grayish yellow powder, containing no sulphur, oxygen, nor hydrogen, and not decomposed by a low red heat. By a strong red heat it is dissipated, yielding a mixture of 3 vol. cyanogen to 1 vol. nitrogen.

This residue may be viewed as a cyanide of nitrogen $N\,Cy_3 = C_6\,N_4$, and as it plays the part of a radical, analogous to cyanogen, it is called mellone, and has the symbol Me. Its production from sulphocyanogen is easily explained: $4\,(C_2\,NS_2) = 2\,CS_2 + S_4 + C_6\,N_4$. If the orange-yellow compound which yields it be thrown into melted sulphocyanide of potassium the mellone actually seizes the potassium, expelling the sulphocyanogen, which is resolved into bisulphuret of carbon, sulphur, cyanogen, and nitrogen, all of which escape with effervescence. This is because mellone is not only a powerful radical, but also capable of resisting a strong heat.

XI. MELLONE. $Me = C_6\,N_4 = 92{\cdot}94$.

The preparation of this radical by the action of heat on impure sulphocyanogen, has been described above. It may also be obtained by heating to low redness the sulphocyanide of ammonium, as will be explained below. It appears as a grayish-yellow powder, which is capable of combining directly with potassium when heated with it, and of decomposing sulphocyanide of potassium, as before-mentioned. In both cases it forms a fusible, soluble, crystallisable salt, mellonide of potassium. When to the solution of this salt an acid is added, it causes a white gelatinous precipitate, which is an acid, sparingly soluble in water, the hydromellonic acid.

Hydromellonic Acid—$Me\,H = C_6\,N_4, H$—is best formed by mixing a hot solution of mellonide of potassium with strong hydrochloric acid, when, on cooling, hydromellonic acid is deposited as a snow-white powder. It is somewhat soluble in hot water, sparingly so in cold; it is a strong acid, and with acetate of potash, produces mellonide of potassium, displacing the acetic acid. If, however, a saturated hot solution of the mellonide be mixed with acetic acid, half the potash is removed, and on cooling, crystals of an acid salt are deposited, which, in the case of a hydrogen acid, is very unusual. It is possible, however, that hydromellonic acid may be bibasic, which would account for the fact of its forming an acid salt.

Mellonide of Potassium—Me, K $= C_6 N_4$, K—occurs as an accidental product in the making of sulphocyanide of potassium. It is best obtained by fusing at a low red heat, in a covered iron crucible, dried ferrocyanide of potassium, with about half its weight of sulphur, and adding, towards the end of the fusion, about 5 per cent. of dried carbonate of potash. The cooled mass is boiled with water, and the filtered solution concentrated, till, on cooling, it forms a semi-solid mass of minute needles, which are purified from sulphocyanide by washing with alcohol, in which the mellonide is insoluble. The mellonide may also be obtained by adding mellone to fused sulphocyanide of potassium, when, by the decomposition of the sulphocyanogen, an additional quantity of mellone is formed. In the first process, also, a portion of mellone is formed by the action of heat on the sulphocyanide of iron, produced at the commencement of the fusion; and this mellone acts, as in the second process, on the sulphocyanide of potassium, giving rise, in so doing, to an additional amount of mellone: hence, the advantage of adding some carbonate of potash, to prevent any loss of mellone. Finally, mellonide of potassium may also be prepared by adding 2 parts of dry subsulphocyanide of copper to 3 of fused sulphocyanide of potassium.

Mellonide of potassium is soluble in water, insoluble in alcohol. It has a bitter taste, and its crystals contain 5 eq. of water, of which 4 eqs. are expelled at 212°. When acted on by hydrochloric acid, it yields hydromellonic acid; when, by acetic acid, it gives the acid salt above-mentioned. By the action of mellonide of potassium on the salts of baryta, strontia, lime or magnesia, the mellonides of barium, &c. are obtained as sparingly soluble salts, which crystallise in fine needles.

By boiling mellonide of potassium with excess of potash, ammonia is given off, and a new salt is formed. This decomposed by acetic acid, yields a white crystalline precipitate, containing no potash, probably a new acid. When dilute solution of mellonide of potassium is acted on by strong hydrochloric acid, and boiled till the hydromellonic acid is re-dissolved, the liquid, on cooling, deposits cyanuric acid, and contains sal ammoniac. Hydromellonic acid Cy_3 NH, with 3 eq. of water H_3 O_3, and 1 eq. oxygen, yields dry cyanuric acid, Cy_3 O_3, and oxide of ammonium, $NH_4\,O$. The equivalent of oxygen is probably derived from the atmosphere; but this decomposition, as well as the preceding, requires minute investigation.

PRODUCTS OF THE DISTILLATION OF SULPHOCYANIDE OF AMMONIUM.

As an appendix to sulphocyanogen and its derivative mellone, we may consider the remarkable results of the action of heat on sulphocyanide of ammonium, $NH_4,\,C_2\,NS_2$.

When this salt is heated in a retort, there are given off as gases or vapours, bisulphuret of carbon, ammonia, and sulphuretted hydrogen, the two latter partly combined as sulphuret of ammonium:

4 eq. Sulphocyanide of Ammonium . . may yield	$=C_8\ N_8\ S_8\ H_{16}$
2 eq. Bisulphuret of Carbon . . .	$=C_2\ S_4$
4 eq. Ammonia	$=N_4\ H_{12}$
4 eq. Sulphuretted Hydrogen . . .	$=S_4\ H_4$
1 eq. Mellone	$=C_6\ N_4$
	$C_8\ N_8\ S_8\ H_{16}$

Such is, in fact, the result of the action of a strong heat on the salt, mellone alone remaining in the retort. But if a more moderate heat be employed, a gray residue is left, containing the elements of mellone with those of ammonia. If this crude residue be dissolved in boiling potash, and the solution quickly filtered, there is deposited, on cooling, a heavy white powder, which is the chief product of the distillation of the sulphocyanide, in a state of purity. It has been called Melam, and its formula is $C_{12}\,N_{11}\,H_9 = 2\,C_6\,N_4 + 3\,NH_3$, or 2 eq. mellone and 3 eq. ammonia.

When the crude melam is acted on by oil of vitriol it dissolves with the aid of a gentle heat, and if water be added, and the whole boiled till the addition of carbonate of ammonia causes no further precipitate, the liquid, on cooling, deposits a large quantity of cyanuric acid, and is found to contain sulphate of ammonia. Now, as mellone, by the action of acids or alkalies, yields cyanuric acid and ammonia, it is easy to see that melam should do the same, $C_{12}\,N_{11}\,H_9$; that is, melam is equal to 2 eq. mellone $C_{12}\,N_8$, and 3 eq. ammonia $N_3\,H_9$; and if we represent mellone by $Cy_3\,N$, melam will be $2\,Cy_3\,N + 3\,NH_3$. Now let us add 12 eq. of water, and $2\,Cy_3\,N + H_{12}\,O_{12} = 2\,(Cy_3\,O_6,\,H_3) + 2\,NH_3$, and adding the 3 eq. of ammonia already present in melam, we have 2 eq. hydrated cyanuric acid, $2\,(Cy_3\,O_6,\,H_3)$, and 5 eq. ammonia, $5\,NH_3$, as the final results from 1 eq. melam and 12 eq. water, under the influence of acids and heat.

When melam is acted on by boiling with potash, a series of new compounds is obtained. The first is melamine, which is deposited in crystals when the alkaline solution cools. Melamine contains no oxygen, but is an artificial organic base, neutralising acids, and forming salts. Its formula is $C_6\ N_6\ H_6 = C_6\ N_4 + N_2\ H_6$; that is, it contains the elements of 1 eq. mellone, and 2 eq. ammonia.

The second new body is obtained as a white powder, when the alkaline solution which has deposited melamine, is supersaturated with acetic acid. It is called ammeline, and is also a base, although weaker than melamine. Its formula is $C_6\ N_5\ H_5\ O_2 = C_6\ N_4 + N H_3 + 2\ H O$, or 1 eq. mellone, 1 eq. ammonia, and 2 eq. water. It forms a crystallisable salt with nitric acid.

It may here be observed, that melam, $C_{12}\ N_{11}\ H_9$, with 2 eq. water, $H_2\ O_2$, contains the elements of 1 eq. melamine, $C_6\ N_6\ H_6$, and 1 eq. ammeline, $C_6\ N_5\ H_5\ O_2$.

When either melamine or ammeline is dissolved in strong sulphuric acid, or melam in nitric acid, and the solution mixed first with two vol. of water, and then with four of alcohol, a white powder is obtained, resembling ammeline, but having the formula $C_{12}N_9H_9O_6 = 2\ C_6N_4 + N\ H_3 + 6\ H\ O$, or 2 eq. mellone, 1 eq. ammonia, and 6 eq. water. It is called ammelide, and has rather the characters of an acid than of a base.

Melamine, by the action of hydrochloric acid, aided by heat, is transformed into ammeline, giving off ammonia, while water is taken up. $C_6N_6H_6 + H_2O_2 = C_6N_6H_8O_2$, and $C_6N_6H_8O_2 - N\ H_3 = C_6N_5H_5O_2$.

Melam also, when treated in the same way, yields ammeline and ammonia. $C_{12}N_{11}H_9 + H_4O_4 = C_{12}N_{11}H_{13}O_4$; and $C_{12}N_{11}H_{13}O_4 - N\ H_3 = C_{12}N_{10}H_{10}O_4 = 2\ (C_6N_5H_5O_2)$.

All these substances may be resolved, by the action of acids, into cyanuric acid and ammonia. It appears that they are all, that is, melam, melamine, and ammeline, first converted into ammelide, and that ammelide is the source of the cyanuric acid and ammonia.

It is obvious that they are all closely related to each other, and to cyanuric acid. That they are also related to mellone is probable, because when heated they leave a yellow residue, which is converted by a stronger heat into cyanogen and nitrogen; which, in short, is mellone. All these compounds may be represented as tribasic cyanurate of ammonia, minus water, or water and ammonia. Thus,

1 eq. anhydrous cyanurate of ammonia, $Cy_3\ O_3,\ 3\ N\ H_3 = C_6\ N_6\ H_9\ O_3$
Minus 3 eq. water . . . . $= H_3\ O_3$

Yields 1 eq. melamine . . . . . . $= C_6\ N_6\ H_6$

1 eq. anhydrous cyanurate of ammonia . . . . $=C_6\ N_6\ H_9\ O_3$

$$\left.\begin{array}{l}\text{Minus 1 eq. water} = H\,O\\ \text{,, 1 eq. ammonia} = H_3\ N\end{array}\right\} N\,H_4\,O \quad .\ . = \quad N\ H_4\ O$$

Yields 1 eq. ammeline . . . . . . $=C_6\ N_5\ H_5\ O_2$

2 eq. anhydrous cyanurate of ammonia . . $=C_{12}\ N_{12}\ H_{18}\ O_6$

$$\left.\begin{array}{l}\text{Minus 1 eq. ammonia} = N\,H_3\\ \text{,, 6 eq. water} = H_6\,O_6\end{array}\right\} \ .\ \ .\ . = \quad N\ H_9\ O_6$$

Yields 1 eq. melam . . . . . $=C_{12}\ N_{11}\ H_9$

2 eq. anhydrous cyanurate of ammonia . . . $=C_{12}\ N_{12}\ H_{18}\ O_6$

Minus 3 eq. ammonia . . . . . . $= N_3\ H_9$

Yields 1 eq. ammelide . . . . . $=C_{12}\ N_9\ H_9\ O_6$

When the mass remaining in the retort when urea is heated, and formerly believed to be cyanuric acid or cyanurate of ammonia, is acted on by acids, it yields cyanuric acid, and ammonia is found in the solution; but if it be boiled with water, an insoluble snow-white powder is obtained, which agrees with ammelide in almost all its properties. Its formula, however, is $C_6\ N_4\ H_4\ O_4$, and it may also be derived from cyanurate of ammonia, as follows:—

$$\left.\begin{array}{l}\text{1 eq. anhydrous tribasic cyanurate of ammonia,}\\ \qquad Cy_3\ O_3, 3\,N\,H_3\end{array}\right\} = C_6\ N_6\ H_9\ O_3$$

Minus 2 eq. ammonia . . . . $= N_2\ H_6$

and $C_6\ N_4\ H_3\ O_3$

Plus 1 eq. water . . . . $= H\ O$

Yields 1 eq. of the new product from urea $= C_6\ N_4\ H_4\ O_4$

This product, therefore, is intermediate between ammelide and cyanuric acid.

To be transformed into hydrated cyanuric acid, it has only to lose 1 eq. ammonia, and to gain 2 eq. water. Its formation from urea is very easily understood; for 4 eq. urea, minus 2 eq. carbonic acid and 4 eq. ammonia, will give this compound:—

4 eq. urea . . . . . . $C_8\ N_8\ H_{16}\ O_8$

$$\left.\begin{array}{l}\text{Minus 2 eq. carbonic acid } C_2\,O_4\\ \text{,, 4 eq. ammonia} \qquad N_4\,H_{12}\end{array}\right\} = C_2\ N_4\ H_{12}\ O_4$$

1 eq. of the new compound . . $C_6\ N_4\ H_4\ O_4$

In order to render still more obvious the relation of these compounds, melam excepted, to cyanuric acid and among each other, let us express the hypothetical compound NH by M_2, M, therefore, standing for $\frac{1}{2}$ eq. NH. We then have—

Melamine, $C_6\ N_6\ H_6$ . . . . . $= Cy_3\ M_6 + H_3$

Ammeline, $C_6\ N_5\ H_5\ O_2$ . . $= Cy_3 \left\{ \begin{matrix} M_4 \\ O_2 \end{matrix} \right. + H_3$

Ammelide, $C_6\ N_{4\frac{1}{2}}\ H_{4\frac{1}{2}}\ O_3$ . . $= Cy_3 \left\{ \begin{matrix} M_3 \\ O_3 \end{matrix} \right. + H_3$

The new compound from urea, $C_6\ N_4\ H_4\ O_4 = Cy_3 \left\{ \begin{matrix} M_2 \\ O_4 \end{matrix} \right. + H_3$

And cyanuric acid . . . $= Cy_3\ O_6 + H_3$

Here we see the change in properties accompanying the gradual substitution of M for O. At one end of the series is melamine, a base, containing no oxygen; at the other, cyanuric acid, a highly oxygenised acid; while ammeline is a weak base, and the remaining two are neutral, or have a tendency, but a very slight one, to acid properties.

Before quitting these compounds, it is proper to point out that as sulphocyanic acid corresponds to cyanic acid, sulphur being substituted for oxygen, so sulphocyanide of ammonium corresponds precisely in the same way to urea; for urea is $C_2\ N_2\ H_4\ O_2$, and sulphocyanide of ammonium is (see above) $C_2\ N_2\ H_4\ S_2$. That this analogy is not imaginary we have seen in the similarity of the action of heat on both.

In the case of urea, 4 eq. . . . . . . $= C_8\ N_8\ H_{16}\ O_8$

$$\left.\begin{array}{ll} \text{yield 2 eq. carbonic acid, } C_2\ O_4 & \\ \text{and 4 eq. ammonia,} & N_4\ H_{12} \end{array}\right\} \ldots = C_2\ N_4\ H_{12}\ O_4$$

Leaving 1 eq. of the new body . . . $= C_6\ N_4\ H_4\ O_4$

In the case of sulphocyanide of ammonium, 4 eq. $= C_8\ N_8\ H_{16}\ S_8$

$$\left.\begin{array}{ll} \text{yield 2 eq. bisulphuret of carbon, } C_2\ S_4 & \\ \text{and 4 eq. ammonia,} & N_4\ H_{12} \end{array}\right\} = C_2\ N_4\ H_{12}\ S_4$$

Leaving 1 eq. mellone + 4 eq. sulphurreted hydrogen $= C_6\ N_4 + H_4\ S_4$

The analogy only fails here in the fact, that the elements $C_6 N_4 H_4 S_4$, instead of uniting, as $C_6 N_4 H_4 O_4$ do, to form one compound, are resolved into two, namely, mellone and sulphuretted hydrogen. Of course the substance from urea may be viewed as compound of 1 eq. mellone and 4 of water; and it may possibly hereafter be resolved into those substances.

When mellone is boiled with nitric acid a new acid is formed, crystallising in octohedrons, which, when re-dissolved in water, form pearly scales. Liebig, who alone has studied it, found its formula and all its reactions exactly like those of cyanuric acid, and called it cyanilic acid: 1 eq. mellone and 6 eq. water, $C_6 N_4 + H_6 O_6$, are equal to 1 eq. cyanilic (or cyanuric) acid, and 1 eq. ammonia $(C_6 N_3 O_6, H_3) + NH_3$. Further experiments are required to establish cyanilic acid as an independent acid.

Having now concluded our sketch of the compounds derived from that of sulphur and cyanogen, it only remains to mention, that cyanogen forms one or two compounds with sulphuretted hydrogen, and that sulphocyanic acid forms a compound with the same gas. These compounds, however, are as yet too little known to permit of their being clearly laid down.

Cyanogen does not form any compound of importance with phosphorus or the remaining metalloids. But there is a very interesting and important series of compounds, in which we may conceive, with some probability, a radical to exist, formed of the elements of cyanogen and those of oxalyle (see p. 276), or carbonic oxide, $C_2 O_2$. This is the series of compounds derived from uric acid, and consequently closely connected with urea, which we have seen to be derived from cyanate of ammonia, and, through cyanic acid, from cyanuric acid, which connects it again with mellone, melam, and sulphocyanogen.

We shall first briefly describe the uric acid itself, as the starting point of an extensive series of products. The radical supposed to exist in these compounds will be better understood if described after we have become acquainted with them.

CYANOGEN WITH CARBONIC OXIDE.

XII. Uryle.

1. Uric Acid. $C_{10} N_4 H_4 O_6 = C_{10} N_4 H_3 O_5 + HO$.

Syn. *Urilic Acid.—Lithic Acid.*—Occurs in small quantity in the healthy urine of man and quadrupeds, and in much larger quantity in the urine of birds, whether carnivorous or herbivorous, as in the pigeon and hawk tribes. In the urine of birds it forms the white part, in the form of urate of ammonia, and it is still found as such in guano—a substance produced by the long-continued action of the air on the urine (or excrement, for they are voided together) of sea-fowl. The only excrement of serpents, as, for example, of the boa constrictor, is a white semisolid mass, which soon dries, and is pure urate of ammonia. In serpents, which are all carnivorous, it is very remarkable that the whole excreta (except occasionally hair and feathers, which pass undigested), should take the form of urate of ammonia. In diseased urine, uric acid is often deposited on cooling, and generally of a reddish colour ; it also constitutes the most frequent form of gravel and of calculus, when deposited within the bladder. Urate of soda is found in the chalk stones of gouty patients ; and it is well known that gout is a disease closely allied to calculus of this kind.

It is best obtained from the excrement (or urine) of the boa, which is powdered, and disssolved in 40 parts of boiling water by the gradual addition of caustic potash, till the liquid is decidedly alkaline. The uric acid forms urate of potash, which dissolves, while the ammonia escapes. The hot liquid, being filtered to separate impurities (and with the above proportion of water it filters rapidly, while with less it crystallises on the filter and chokes it up), is mixed with a decided excess of hydrochloric acid, when the uric acid is set free, and being insoluble, is deposited, at first as a very bulky gelatinous hydrate, which in a few minutes spontaneously loses water and shrinks into a crystalline heavy precipitate. This is well washed with cold water and dried in the air, when it forms a shining powder, composed of distinct but minute crystals. If made from a cold saturated solution of urate of potash, the crystals are much larger, but contain 17·5 per cent.; in this case 4 eq. of water are expelled at 212°, leaving the same substance as that precipitated from a hot solution, which, when dried in the air, loses no weight at 212°. The latter is $C_{10}N_4H_3O_5 + HO = \overline{Ur} + HO$; the large crystals are a hydrate, $\overline{Ur}, HO + 4$ aq.

If pure white fragments of the urine of the boa have been used, the above simple process yields uric acid chemically pure, even when the solution in potash has had a decided yellow colour. This uric acid is snow white, and is entirely dissipated by heat, leaving no trace of ashes. But if the boa's urine have been impure, or if calculi have been employed to yield uric acid, in both of which cases the alkaline solution is brown, often very dark, and yields a coloured uric acid, or again if we wish to extract uric acid from guano, we must first purify the urate of potash by evaporating the alkaline solution till it crystallises in a mass, or passing carbonic acid through it to neutralise the free potash, when the urate of potash is deposited, and is washed on a filter with cold water, in which it is very sparingly soluble, till it is quite white. It is then dissolved in boiling water, and decomposed by hydrochloric acid as before. I have described thus minutely the preparation of pure and colourless uric acid, because none of the very interesting products derived from it can be obtained if we employ uric acid with even a very slight tinge of colour. The presence of a mere trace of the colouring matter of urine I have found to exert a most remarkable influence on the oxidation of uric acid by nitric acid, an influence which I can only compare to that of a ferment in causing a peculiar decomposition to take place.

Uric acid requires 15000 parts of cold and nearly 2000 of hot water for solution, and its solution reddens litmus. It forms salts with bases, especially with the alkalies and alkaline earths, all of which are insoluble or sparingly soluble. Urate of potash, the most soluble of them, requires 85 parts of boiling water, but less if free potash be added. The urate of soda is still less soluble, requiring 124 parts of hot water. The urate of ammonia, a frequent form of calculus, is very sparingly soluble, requiring 243 parts of hot and 1727 of cold water. These are the only urates of any importance.

PRODUCTS OF THE OXIDATION OF URIC ACID.

Uric acid is very permanent under ordinary circumstances, but is readily oxidised by powerful oxidising agents, such as peroxide of lead, peroxide of manganese, permanganate of potash, and nitric acid.

1. *Oxidation of uric acid by peroxide of lead.* If uric acid be mixed with twenty parts of boiling water, and peroxide of lead added in small portions to the liquid kept boiling, the brown colour of the oxide disappears, and a heavy white powder is formed. When we have added about two parts of the oxide for one of uric acid, or, at all events, when the oxide begins not to lose its brown colour, the hot liquid is to be filtered, and on cooling it deposits a number of hard brilliant white crystals, of which more are obtained on evaporation. The mother liquid at last crystallizes in a mass of very soluble prismatic crystals. These last are pure urea: the first crystals are Allantoine, and the powder is oxalate of lead, mixed with a little carbonate, and with the excess of peroxide. Hence, the products of this oxidation are, Urea, Allantoine, and Oxalic Acid. After describing allantoine, we shall be able to explain the reaction.

Allantoine.—$C_4 N_2 H_3 O_3$.—Syn. *Allantoic Acid.*—This body was first observed in the allantoic fluid of the fetal calf, which is, in fact, the urine of the fetal animal. When this fluid is evaporated, it deposits crystals of allantoine, formerly called allantoic acid, which, however, is not an acid. Its occurrence in the allantoic fluid, that is, as an ingredient in urine;

and its artificial production from uric acid by a process of oxidation, are facts of very great interest when viewed in connection. It is best obtained from uric acid, as above described. It is a very indifferent, or neutral substance, and forms few compounds; only one, with oxide of silver, has been described, the formula of which is $C_8N_4H_5O_5 + AgO =$ 2 eq. allantoine, minus 1 eq. water, and plus 1 eq. oxide of silver.

When boiled with alkalies, it is resolved into ammonia which escapes, and oxalic acid which combines with the alkali. In fact, both allantoine, $C_4N_2 + H_3O_3$, and oxalate of ammonia, $C_2O_3 + N\,H_3$, may be represented as formed of cyanogen and water, and it is obvious that the addition of 3 eq. of water, to 1 eq. of allantoine gives $C_4N_2 + H_6O_6 = 2\,(C_2N\,H_3O_3)$.

We can now explain the formation of allantoine.

1 eq. Uric acid			$=C_{10}\,N_4\,H_4\,O_6$
Plus 2 eq. oxygen (from 2 eq. $Pb\,O_2$)	$=O_2$	$\Big\}\,H_3\,O_5=$	$H_3\,O_5$
and 3 eq. water . . .	$H_3\,O_3$		
Together			$=C_{10}\,N_4\,H_7\,O_{11}$
Are equal to 1 eq. urea			$=C_2\,N_2\,H_4\,O_2$
2 eq. oxalic acid			$=C_4\,O_6$
1 eq. allantoine			$=C_4\,N_2\,H_3\,O_3$
Together			$=C_{10}\,N_4\,H_7\,O_{11}$

Or in the form of an equation,

$$C_{10}\,N_4\,H_4O_6 + O_2 + H_3\,O_3 = C_2\,N_2\,H_4\,O_2 + 2\,C_2\,O_3 + C_4\,N_2\,H_3\,O_3$$

That allantoine is closely related to uric acid and urea further appears from the fact, that 1 eq. uric acid, 1 eq. urea, and 1 eq. water, added together, are exactly equal to the sum of 3 eq. allantoine. $C_{10}N_4H_4O_6 + C_2N_2H_4O_2 + H\,O = C_{12}N_6H_9O_9 = 3\,(C_4N_2H_3O_3)$.

2. *Oxidation of uric acid by peroxide of manganese.* This is performed much as the preceding, and there appear to be produced compounds, partly the same as those from peroxide of lead, partly different. Of the latter, one at least is crystallisable, but has not been sufficiently examined. The subject requires investigation.

3. *By permanganate of potash.* In this oxidation also, some products appear, which are obtained by peroxide of lead; such as urea, and, in some forms of the experiment at all events, oxalic acid; but I have also observed the formation of a new acid, containing nitrogen, the precise nature and composition of which is not yet ascertained.

4. *By nitric acid.* This mode of oxidation of uric acid has been minutely studied by Liebig and Wöhler, and they have shown that it yields a very large number of new and important products, among which is again found urea, and also, under certain circumstances, oxalic acid. The changes are best traced when colourless nitric acid of a moderate concentration, of Sp.G. 1·3 or 1·25 for example, is employed.

1. *Alloxan.* When uric acid is added, in small portions, to this acid, it is dissolved with a gentle and uniform effervescence, due to the escape of pure carbonic acid and nitrogen gases, without any trace of the red vapours of nitrous acid. Heat is also developed, so that no external heat is required, and it may even be necessary to moderate the reaction by placing the vessel in cold water. If too much uric acid be added at once, or if the mixture be allowed to get too hot, a violent reaction ensues, accompanied by copious red fumes, after which the experiment cannot succeed, and must be recommenced with fresh materials. The presence of a trace of the colouring matter of the urine infallibly causes this violent reaction, even with a much weaker nitric acid, and thus prevents us from obtaining the desired result, even to a small extent. In all these cases, the whole seems to be converted into oxalate and carbonate of ammonia. When the operation is properly managed, and a little practice makes it quite easy, there appear, in the warm liquid, after a certain quantity of uric acid has been dissolved, granular crystals of the new compound, alloxan. If a little more uric acid be added, it is still dissolved, and when the warm liquid (at about 120°) contains a good many crystals, it is allowed to cool, when the quantity of crystals greatly increases. They are now thrown on a filter stopped with asbestus, and when they have drained, the acid liquor still in their pores is displaced by a little ice-cold water, which is added till the droppings altogether, with the liquid first filtered, have exactly the original bulk of liquid. (This liquid is again treated as before with uric acid, the crystals again collected and washed with a little cold water, and this operation may be repeated always four, occasionally five times, with the same acid, yielding five crops of crystals, and preserving the mother liquor, of which hereafter.) The crystals are now dissolved on the funnel with water at 120°, and the filtered solution evaporated at that or even a lower temperature, till, on being set aside, it deposits large transparent crystals of hydrated alloxan, which are chemically pure. The mother liquid of these crystals, being gently evaporated, yields more, and the final mother liquid, which is now rather acid, from nitric acid, is added to the original acid mother liquor, to be used for other purposes.

By the above process, I have constantly obtained, without difficulty, upwards of 90 parts of hydrated alloxan, quite pure, from 100 of uric acid, besides what remains in the mother liquid, and cannot be extracted in that form.

The crystals of hydrated alloxan, when heated to 212° lose about 27 per cent. of water, = 6 eq. The dry or anhydrous alloxan, which may also be obtained in crystals when a saturated solution is evaporated in a warm place, is composed of $C_8N_2H_4O_{10}$, which explains its formation from uric acid; for $C_{10}N_4H_4O_6 + O_2 + H_4O_4 = C_8N_2H_4O_{10} + C_2N_2H_4O_2$: that is, uric acid, *plus* 2 eq. oxygen and 4 eq. water, yields 1 eq. alloxan and 1 eq. urea.

The urea, when formed, is in contact with hyponitrous acid (derived from nitric acid by the separation of 2 eq. oxygen), and is immediately decomposed by it, yielding oxide of ammonium, which combines with some free nitric acid, carbonic acid, and nitrogen, which two last escape as gases. $C_2N_2H_4O_2 + N\,O_3 = N\,H_4, O + 2\,C\,O_2 + N_2$. At the end of the operation, therefore, the acid liquid, which has deposited crystals of alloxan, contains nothing but alloxan, nitrate of ammonia, and free nitric acid. We may therefore express the final result as follows: $C_{10}N_4H_4O_6 + 2\,(H\,O, N\,O_5) + 2\,H\,O = C_8N_2H_4O_{10} + (N\,H_4O, N\,O_5) + 2\,C\,O_2 + N_2$.

Alloxan is very soluble in water, also in alcohol. Its solution stains the skin pink, and gives to it a heavy sickly odour. Its taste is peculiar and almost acidulous; but, although it reddens litmus, it has not the chemical characters of an acid. It is a very remarkable substance, from the numerous transformations which it undergoes, when subjected to the action of different re-agents.

By the action of soluble fixed alkalies, it is converted into a powerful acid, *alloxanic acid:* by the action of ammonia it yields another acid, *mykomelinic acid;* boiled with peroxide of lead, it is converted into *urea* and *carbonic acid;* by boiling with nitric acid it is changed into a new and powerful acid, *parabanic acid;* by the action of sulphuretted hydrogen and other deoxidising agents, it yields a new compound *alloxantine;* with hydrosulphuret of ammonia it gives a new salt called *dialurate of ammonia;* with sulphurous acid it combines, forming a compound acid, *alloxano-sulphurous* acid: and with sulphite of ammonia it forms another new salt called *thionurate of ammonia.* Such are the compounds formed by the direct action of re-agents on alloxan; but many others are produced by the action of re-agents on these, singly or jointly. Thus, when alloxan and alloxantine are both present in a hot solution, ammonia causes the development of a deep purple colour, and the deposition, on cooling, of the gold green crystals of *murexide;* acids acting on thionurate of ammonia produce *thionuric acid*, *uramile*, and *uramilic acid ;* acids acting on murexide, produce *murexan;* acids acting on dialurate of ammonia separate *dialuric acid;* ammonia, acting on parabanic acid, converts it into a new acid, *oxaluric acid;* and by the action of heat on alloxanate of baryta another new acid, *mesoxalic acid*, is produced. We shall endeavour briefly to trace the formation and the relations of these remarkable products.

2. *Alloxanic Acid.*—Its formula $C_8 N_2 H_2 O_8 + 2HO$. It is therefore isomeric with alloxan, and differs from it in this, that 2 eq. water have become basic, and replaceable by metallic oxides. It is a bibasic acid. It is formed when solution of alloxan is mixed with barytic water, as long as the white precipitate first formed redissolves with a gentle heat. When it begins to be permanent, a drop or two of alloxan is added to clear all up ; and on cooling, alloxanate of baryta is deposited in small white crystals. From this salt the acid is obtained by adding sulphuric acid, so as to separate all the baryta. The acid solution on evaporating yields crystals of alloxanic acid. The acid, when neutralised by ammonia, forms, with nitrate of silver, a white precipitate, which, when boiled, becomes yellow, and is reduced with effervescence. When the solutions of its salts, with baryta, lime, and strontia, are boiled they become turbid, depositing carbonates, while urea and a mesoxalate remain dissolved. The formula of the alloxanates is $C_8 N_2 H_2 O_8, 2MO + aq$.

3. *Mesoxalic acid.* Obtained, in combination with baryta, by boiling alloxanate of baryta ; or combined with oxide of lead, by adding alloxan in solution, to a boiling solution of acetate of lead. The baryta salt is pale yellow, and sparingly soluble ; the lead salt white and insoluble. The former is $C_3 O_4 \left\{ \begin{matrix} BaO \\ HO \end{matrix} \right.$, the latter $C_3 O_4, 2PbO$. The acid may be obtained from either of these salts ; it crystallises, is very sour, and is probably bibasic, and has, also probably, the formula $C_3 O_4, 2HO$. In that case, the anhydrous acid is very remarkable as a new compound of carbon and oxygen, of the same class as mellitic and oxalic acids ; hence the name. It is characterised by forming, when neutralised by ammonia with nitrate of silver, a yellow precipitate, which, when heated, is reduced with brisk effervescence. This is evidently the cause of the reaction of alloxanic acid, above mentioned, with nitrate of silver. Mesoxalic acid deserves and requires a very careful investigation. Its formation from alloxan or alloxanic acid, if its formula be C_3O_4, is very easily explained : for 1 eq. alloxan, *minus* 1 eq. urea, gives 2 eq. mesoxalic acid. $C_8 N_2 H_4 O_{10} - C_2 N_2 H_4 O_2 = C_6 O_8 = 2C_3 O_4$.

4. *Mykomelinic acid.* $C_8 N_4 H_5 O_5$. Is formed when

ammonia acts on solution of alloxan ; when a yellowish gelatinous precipitate of mykomelinate of ammonia soon appears. This boiled with dilute sulphuric acid yields a similar yellowish precipitate, which, when dry, forms a powder sparingly soluble in cold, more readily in hot, water. It is decidedly acid. It is formed of the acid by the reaction of 2 eq. of ammonia on 1 eq. alloxan. $C_8 N_2 H_4 O_{10} + 2NH_3 = C_8 N_4 H_5 O_5 + 5HO$. It would appear to differ from allantoine, only by 1 eq. of water: for 2 eq. of allantoine are $C_8 N_4 H_6 O_6$.

5. *Parabanic acid.* $C_6 N_2 O_4 + 2HO$. Is formed when alloxan or uric acid is heated with an excess of nitric acid, and the solution concentrated until on cooling it forms a soft crystalline mass. This is dried on a tile, and the dry crystals are purified by solution in hot water, filtration, and recrystallisation. A large quantity of parabanic acid may easily be obtained from the acid mother liquors of alloxan. When pure, the acid is beautifully white and crystallised, very acid, and very soluble. It is characterised by its great permanence in the free state, for it may be boiled with nitric acid, as its preparation shows, and at the same time by its extreme proneness to change in contact with bases. Thus, if neutralised with ammonia in the warm solution, it deposits, on cooling, a crystallised salt, which is oxalurate of ammonia. The same change takes place with all bases except oxide of silver, so that the parabanate of silver is the only salt of this very powerful and remarkable acid which can be obtained. To be converted into oxaluric acid, parabanic acid only requires 3 eq. of water. The production of parabanic acid is very simple. 1. From uric acid. $C_{10} N_4 H_4 O_6 + O_4 + H_2 O_2 = C_2 N_2 H_4 O_2 + 2CO_2 + C_6 N_2 O_4, 2HO$. 2. From alloxan. $C_8 N_2 H_4 O_{10} + O_2 = 2CO_2 + 2HO + C_6 N_2 O_4, 2HO$.

6. *Oxaluric Acid.* $C_6 N_2 H_3 O_7 + HO$. Formed by the action of bases on parabanic acid. $C_6 N_2 O_4 + KO + 3HO = C_6 N_2 H_3 O_7, KO$. The acid is obtained by adding dilute sulphuric acid to a hot saturated solution of oxalurate of ammonia, prepared by the action of ammonia on parabanic acid. On cooling, the oxaluric acid is deposited as a heavy white powder. When long boiled in water, it is decomposed into oxalate of urea and free oxalic acid. In fact, it contains the elements of 2 eq. oxalic acid and 1 eq. urea. $2C_2 O_3 + C_2 N_2 H_4 O_2 = C_6 N_2 H_3 O_7, HO$. It is also characterised by forming with oxide of silver a white salt, which dissolves in hot water, and crystallises beautifully on cooling.

The *oxalurate of ammonia*, $NH_4 O + C_6 N_2 H_3 O_7$, is formed whenever a solution of alloxan, or alloxantine in water, or of uric acid in nitric acid, is evaporated with excess of ammonia, and where colouring matter is present, as when ammonia is made to act on the acid in the mother liquors of alloxan, the oxalurate is often deposited in radiated hemispherical concretions, which sometimes attain the size of an inch or two in diameter, and are very hard. When decolorised by animal charcoal, it forms small, soft, flexible needles. I have found that this salt, when exposed to heat in a retort, yields ammonia, hydrocyanic acid, and much oxamide, besides water, and perhaps other products, while a dark residue is left.

7. *Thionuric Acid,* $C_8 N_3 H_7 S_2 O_{14} = (C_8 N_3 H_5 O_8, 2 SO_2) + 2 HO$, is formed when sulphite of ammonia, with excess of base, is added to solution of alloxan, and the whole boiled for a few minutes, or until crystals appear in the hot liquid. On cooling it forms a semi-solid mass, from the separation of a large quantity of thionurate of ammonia in beautiful silvery crystals, which are to be washed with cold water, and dried on a tile. From this salt thionurate of lead is prepared, and this, being decomposed by sulphuric acid, yields thionuric acid. The acid is crystallisable, but very soluble. It is bibasic, and contains the elements of 1 eq. alloxan, 1 eq. ammonia, and 2 eq. sulphurous acid, not however as such, for the elements of 2 eq. water have assumed the basic form.

Its most striking character is, that when its solution is heated it becomes turbid from the deposition of a new compound, uramile, and in the liquid *sulphuric* acid may now be found, which was not previously present. $C_8 N_3 H_5 O_8 + 2 SO_2 = C_8 N_3 H_5 O_6 + 2 SO_3$; so that the sulphurous acid obtains oxygen from the rest of the acid, and becomes sulphuric acid, leaving uramile, $C_8 N_3 H_5 O_6$.

Thionurate of Ammonia, $(C_8 N_3 H_5 O_8, 2 SO_2) + 2 NH_4 O + 2$ aq. is formed as above-described. When its solution is mixed with 1 eq. of hydrochloric acid, half the ammonia is removed, and by evaporation we obtain *acid thionurate of ammonia* in minute silky needles. But when the hot solution of thionurate of ammonia is mixed with an excess of acid, the thionuric acid is set free and instantly decomposed, uramile being deposited. Little is known of the other thionurates.

8. *Uramile;* $C_8 N_3 H_5 O_6$; its formation has been described above. It occurs either as a crystalline powder, or in dendritic or feathery crystallisations, of very beautiful aspect. It dissolves in ammonia and potash, and the solution absorbs oxygen; becoming purple, and depositing green crystals of murexide, or of potassium-murexide. When boiled with peroxide of mercury, and a very little ammonia, it is also converted into murexide.

Boiled with caustic potash, or with dilute acids, it is said to yield uramilic acid. Nitric acid re-converts it into alloxan.

9. *Uramilic Acid.* Obtained, by Liebig and Wöhler, by evaporating acid thionurate of ammonia, or uramile, with dilute sulphuric acid; also, it is said, by boiling uramile with potash. It appeared to these chemists as fine prisms, very soluble in water, and its analysis indicated the formula $C_{16} N_5 H_{10} O_{15}$; which might be derived from 2 eq. uramile by the loss of 1 eq. ammonia, and the addition of 3 eq. water. $2 (C_8 N_3 H_5 O_6) + 2 HO - NH_3 = C_{16} N_5 H_{10} O_{15}$. But this acid has not been again obtained, and its existence is still doubtful.

10. *Alloxantine;* $C_8 N_2 H_5 O_{10}$; obtained in large quantity by diluting the acid mother liquid of alloxan with 3 or 4 parts of water, and passing a current of sulphuretted hydrogen through it. In a short time sulphur is deposited, and then white crystals of alloxantine. When a large quantity has formed, it is collected with the sulphur, on a filter, washed with a little cold water, and the filter with its contents then boiled with a large quantity of water. The solution filtered while hot, and with the addition of a few drops of hydrochloric acid, deposits, on cooling, a large crop of pure crystals of alloxantine. The acid liquid, filtered from the first deposit, often, on standing a day or two, deposits a large additional quantity of alloxantine. This always happens, if too much sulphuretted hydrogen has been used; for that converts the alloxantine partially into dialuric acid, which is more soluble, but by absorbing oxygen from the air is reconverted into alloxantine, and thus deposited.

Alloxantine may also be obtained by deoxidising a pure solution of alloxan, either by sulphuretted hydrogen, or by other deoxidising agents; or by heating a solution of alloxan to the boiling point, either by itself or with the addition of dilute mineral acids, when alloxantine is formed and deposited on cooling. But the process above given for converting into alloxantine the alloxan of the acid mother liquor, which cannot be purified by crystallisation, is so productive, and yields alloxantine so pure, that, if we have to prepare alloxan, we need never be at a loss for alloxantine.

The formation of alloxantine from alloxan by sulphuretted hydrogen is easily explained, for these compounds only differ by 1 eq. hydrogen, which the alloxan takes from sulphuretted hydrogen. Oxidising agents, by converting this hydrogen into water, readily reconvert alloxantine into alloxan. $C_8 N_2 H_5 O_{10} + O = HO + C_8 N_2 H_4 O_{10}$.

Alloxantine forms white, hard, brilliant crystals, which never exceed a certain small size. It is very sparingly soluble in cold water, much more so in hot water. Its solution is characterised by giving with solution of baryta a deep violet precipitate, which with excess of baryta, changes to white ; and by instantly reducing nitrate of silver, forming a black powder of silver, the alloxantine passing into alloxan, or oxaluric acid. The crystals of alloxantine, heated to 300°, lose 3 eq. of water.

In the preparation of alloxan, it is necessary, as has been stated, to be very careful that the first solution of the crystals formed in the nitric acid should not be heated too strongly, because, as this solution contains free nitric acid, alloxantine is formed at a certain temperature ; and besides, even a pure solution of alloxan, if boiled, is partly converted into alloxantine. The action of diluted nitric and other mineral acids on alloxan is to produce, from 2 eq. alloxan, 1 eq. alloxantine, 3 eq. oxalic acid, 1 eq. ammonia, and 1 eq. cyanic acid, the latter, with 3 eq. water, producing bicarbonate of ammonia. When solution of alloxan is boiled alone, it is converted into alloxantine, parabanic acid, and carbonic acid. $3\,(C_8\,N_2\,H_4\,O_{10}) = 2\,(C_8\,N_2\,H_5\,O_{10}) + C_6\,N_2\,H_2\,O_6 + 2\,C\,O_2$.

In all these, or in similar cases, the presence and the relative proportion of alloxantine contained in alloxan at any period, may be judged of by the colour of the precipitate formed in baryta. If pure white, no alloxantine is present : if slightly pink, it is present in small quantity ; if deep violet, all, or nearly all, the alloxan has been converted into alloxantine.

It is when both alloxan and alloxantine are present, that the addition of ammonia produces the deep purple colour, and the green crystals, of murexide. When ammonia acts on alloxantine alone, it gives rise to uramile, and, finally, to oxalurate of ammonia.

The most remarkable change which alloxantine undergoes is that caused by the further action of sulphuretted hydrogen. If that gas be passed through a hot solution of alloxantine sulphur is precipitated, and an acid liquid is obtained, which, if neutralised by carbonate of ammonia, forms a salt in soft white silky crystals, the dialurate of ammonia. Alloxantine, by the action of hydrogen, which removes 1 eq. oxygen, is converted into dialuric acid.

11. *Dialuric acid.* $C_8\,N_2\,H_3\,O_7 + HO = C_8\,N_2\,H_4\,O_8$. Produced by the action of sulphuretted hydrogen on alloxantine. $C_8\,N_2\,H_5\,O_{10} + HS = S + 2\,HO + C_8\,N_2\,H_4\,O_8$. It is best obtained, in combination with ammonia, by adding a slight excess of hydrosulphuret of ammonia to a solution of alloxan or alloxantine, when a copious crystalline precipitate appears. This, when boiled, dissolves in the liquid, and on cooling is deposited

in minute silky prisms, which are white, but in drying become pink or even deep red. They should be washed on the filter, first with diluted hydrosulphuret of ammonia, then with alcohol, to which a little hydrosulphuret has been added; and lastly, with pure alcohol; and dried by pressure in blotting-paper, and in the vacuum of the air-pump. They may thus be obtained white, or very nearly so; and when once quite dry, they are permanent. When this salt is dissolved in hot and moderately strong hydrochloric acid, crystals of dialuric acid are deposited on cooling. These crystals resemble somewhat those of alloxantine, but are larger, and not so brilliant. Their solution, and the crystals themselves under water, absorb oxygen, and are soon changed into alloxantine, from which dialuric acid only differs by 1 eq. oxygen and 1 eq. water.

Dialuric acid is a powerful acid. Its salts are insoluble or sparingly soluble, and only permanent in the dry state. The dialurate of ammonia, above described, is the most interesting.

12. *Murexide.* SYN. *Purpurate of ammonia.* Formed, as already mentioned, when ammonia acts on a solution containing both alloxan and alloxantine, which explains its production when ammonia is added to the solution of uric acid in dilute nitric acid, after evaporation to a certain extent: also, when uramile or murexan is boiled, with red oxide of mercury or oxide of silver, in water, with a few drops of ammonia, or when uramile or murexan is dissolved in ammonia and exposed to the atmosphere; and in a great variety of circumstances from all the preceding compounds, or nearly all of them.

On the small scale, 4 grains of alloxantine and 7 grains of hydrated alloxan, are dissolved together in $\frac{1}{2}$ oz. by measure of water by boiling, and the hot solution added to $\frac{1}{6}$ oz. by measure of a saturated or nearly saturated solution of carbonate of ammonia, the latter being cold. This mixture has exactly the proper temperature for the formation of murexide; and it does not, owing to its small bulk, remain too long hot. It instantly becomes intensely purple, while carbonic acid is expelled; and as soon as it begins to cool, the beautiful green and metallic-looking crystals of murexide appear. As soon as the liquid is cold, these may be collected, washed with a little cold water, and dried on filtering-paper. I have obtained them, by the above process, and on this small scale, of from 2 to 3 lines in length. When made with larger quantities, the crystals are always smaller, owing, probably, to some effect of the slower cooling of the larger mass of liquid, as continued heat is not favourable to their formation. If we do not care about having the finest crystals, we may prepare murexide in large quantity by adding solution of alloxan to a boiling solution of alloxantine, and cautiously adding cold solution of carbonate of ammonia, till the mixture has become nearly black, and the green crystals begin to appear. The vessel being removed from the fire, deposits a very large quantity of murexide. In these processes, the residual liquid is still coloured, and is alkaline from excess of ammonia: if kept, it loses the red colour, becomes yellowish, and if evaporated, yields much alloxanate of ammonia in crystals.

Murexide is one of the most beautiful products of chemistry: the crystals are metallic green by reflected light, like the cantharides fly or the gold beetle, and deep red by transmitted light. Their solution is deep purplish red, and they dissolve in potash with the most splendid purplish blue colour that can be imagined; this, however, soon disappears. When their solution is acted on by a dilute mineral acid, it is decolorised, and deposits a shining scaly crystalline powder, of a pale yellow colour, which is murexan. The same compound is obtained when acids are added to the solution of murexide in potash, after the purple tint has disappeared on digestion in a gentle heat.

The composition of murexide is uncertain, and there are different views of its constitution. According to some it is a salt of ammonia; and this view is supported by the fact that, with salts of baryta and oxides of lead and silver, it yields purple salts, which, according to Fritzsche, contain the same acid that in murexide is combined with ammonia, and which may be called purpuric acid. But murexide is not a compound of ammonia with the purpuric acid of Prout, for when that body (murexan) is dissolved in ammonia, it only forms murexide by absorbing oxygen from the air, and yields other compounds at the same time. Again, the action of sulphuretted hydrogen is inconsistent with the view of murexide being a salt of ammonia, and in many of its relations it more resembles a neutral body—such as a compound of amide. Its products of decomposition are very numerous, and altogether the subject is one of much difficulty. Possibly there may be two substances similar in appearance, but distinct in constitution; one a salt of ammonia, the other an indifferent body, or an amidide. The great discrepancy in the results of analysis, as obtained by Liebig and Wöhler on the one hand, and Fritzsche on the other, as well as some differences in the properties ascribed to it by different chemists, lead to some such conclusion. The formula considered by Liebig and Wöhler the most probable, all things considered, but not established, is $C_{12} N_5 H_6 O_8$; another, somewhat less probable, is $C_{20} N_8 H_{10} O_{14}$. Both of these will enable us to account for its production in different circumstances.

The formula of Fritzsche, which agrees with his analysis, is $C_{16}N_6H_8O_{11} = NH_3 + C_{16}N_5H_5O_{11}$. The salt formed with nitrate of silver is, $C_{16}N_5H_5O_{11} + AgO$, which would exhibit the unusual phenomenon of ammonia, instead of oxide of ammonium, being replaced by oxide of silver; and the baryta compound is $C_{16}N_5H_5O_{11} + HO + BaO$. Admitting the formulæ of Fritzsche for the silver and barium compounds to be correct, these are not demonstrated to be salts of purpuric acid: but besides this, his formula for murexide does not enable us to explain its production in any case. In these circumstances, we shall not attempt to explain the formation of murexide, further than to point out, that it appears to require the presence of a compound intermediate between alloxan and alloxantine (the former losing oxygen, the latter gaining it), and of ammonia; and that it is not the only product.

13. *Murexan.* Syn. *Purpuric Acid.* $C_6N_2H_4O_5$? Formed by the action of acids on murexide, but along with several other products. It appears as a shining powder, composed of scales, generally pale yellow, sometimes pale brown, never quite white. It is insoluble in water or nearly so, but the liquid filtered from it has always a peculiar opalescent aspect and play of colours. It dissolves in potash and ammonia, and the solutions become purple, by absorbing rapidly oxygen from the air, and finally deposit green crystals. When boiled with peroxide of mercury, water, and a little ammonia, it yields murexide. It dissolves in oil of vitriol, and is precipitated unchanged by water. In all these characters, except in its external aspect, it coincides entirely with uramile, and it is not impossible that it may be hereafter found to be uramile, disguised by the presence of a foreign substance. For the present, however, its analysis compels us to distinguish it from uramile.

Having now described the numerous products of the oxidation of uric acid by nitric acid, we are prepared to understand the nature of the radical supposed to be common to most of these compounds.

URYLE. $Ul. = C_8N_2O_4 = 4CO + 2C_2N$.

Syn. Cyanoxalic acid. This radical is unknown in the separate form. It contains the elements of four eq. carbonic oxide or 2 eq. oxalyle (C_2O_2), and 2 eq. cyanogen. Hence the name cyanoxalic acid. Assuming it to exist, we have the following series.

Rational formulæ.	Names.	Empirical formulæ.
Ul + 1 eq. urea	= Uric acid	$= C_{10}N_4H_4O_6$
$Ul + O + 5HO$	= Alloxantine	$= C_8N_2H_5O_{10}$

Rational formulæ.	Names.	Empirical formulæ.
$Ul + O_2 + 4\,HO$	= Alloxan	= $C_8\ N_2\ H_4\ O_{10}$
$Ul + 4\,HO$	= Dialuric acid	= $C_8\ N_2\ H_4\ O_8$
$Ul + NH_3 + 2\,HO$	= Uramile	= $C_8\ N_3\ H_5\ O_6$
$Ul + O_2 + 4\,HO + NH_3 + 2\,SO_2$	= Thionuric acid	= $C_8\ N_3\ H_7\ O_{14}\ S_2$

The ready conversion of these compounds one into another is a strong argument for the existence of the radical Uryle. But the rational formulæ above given do not represent what we suppose to be the actual arrangement; they only point out by what simple means, as the addition or removal of oxygen, or ammonia, or water, the elements of the new compounds might be supplied. The other derivatives of uric acid are probably compounds of different radicals: thus, parabanic and oxaluric acids each contain only 6 eq. of carbon, and cannot therefore be compounds of uryle.

APPENDIX TO URIC ACID.

1. *Uric or Xanthic oxide.* This a very rare ingredient of urinary calculi. Its formula is $C_5N_2H_2O_2$, which, taken double, differs from uric acid only by 2 eq. oxyygen. Hence its name of uric oxide. It is soluble in potash and precipitated by acids as a white powder. It dissolves in nitric acid, and the solution evaporated to dryness leaves a yellow residue; hence the name of xanthic oxide. It is said to occur in small quantities in some kinds of guano.

2. *Cystic oxide.* $C_6N\ H_6O_4S_2$. Another very rare form of calculus. It dissolves both in acids and alkalies, and has the characters of an organic base, forming crystalline compounds with acids. It is remarkable from the large quantity of sulphur it contains.

XIII. BENZOYLE. $Bz = C_{14}\ H_5\ O_2$.

This is the radical of Benzoic Acid, of oil of bitter almonds, and of an extensive series of compounds. The radical is not yet known with certainty in the separate form, although a compound exists, having the same composition. (See Benzile.) We shall describe first the benzoic acid, and afterwards the other compounds derived from, or connected with it.

1. Benzoic Acid. $C_{14}\ H_5\ O_3, HO = Bz\ O, HO$, or $Bz\ O_2, H$.

This acid is found in gum benzoin, mixed with some resins; and it also occurs in the urine of herbivorous animals, under certain circumstances. It is also formed by the oxidation of the oil of bitter almonds. It may be obtained from benzoin by sublimation, the powdered gum being gently heated on an iron plate forming the bottom of a broad and short cylinder, the top of which is covered with bibulous paper pasted tightly down to the sides, while another cylinder slides over the upper end of the first, to prevent the escape of the acid. The vapours of the acid, which is very volatile, pass through the paper, and forming crystals, are there retained, falling on its upper surface. The following method, however, is far more productive, as in the process of sublimation some of the acid is always decomposed. Benzoin is dissolved in strong alcohol, and to the hot solution there is added hydrochloric acid in quantity sufficient to precipitate the resin: the whole is then distilled. The benzoic acid passes over under the form of benzoic ether (benzoate of oxide of ethyle); and when the greater part of the liquid has been distilled off, water is added to the residue, and distilled as long as any ether passes over with it. When this ceases, the hot water remaining in the retort is filtered, and on cooling deposits part of the benzoic acid in crystals. The benzoic ether and all the distilled liquors are now treated with caustic potash, until all the ether is decomposed, and the solution, now containing benzoate of potash, is heated to boiling, and supersaturated with hydrochloric acid. On cooling it deposits the benzoic acid in crystals. By this means the whole benzoic acid of the benzoin is obtained.

Benzoic acid forms fine light prismatic crystals, or flexible pearly scales. When pure, it has no smell, but by heat it acquires the odour of benzoin or of vanilla, and as commonly prepared it has a very pleasant odour derived from the presence of some foreign compound which accompanies the acid, and is not easily separated from it. It is very fusible and volatile, and its vapours are very irritating, provoking cough. It is inflammable, burning with smoke. It is sparingly soluble in cold water, more so in boiling water; it dissolves also in alcohol and ether.

With bases it forms salts, many of which are crystallisable. Their general formula is $Bz\,O, M\,O$, or $Bz\,O_2, M$. When the alkaline and earthy benzoates are heated in close vessels, they yield carbonates, while new products distil over, such as benzone, benzole, naphthaline, &c. The benzoate of peroxide of iron, $3\,Bz\,O + Fe_2O_3$, has a reddish white colour, and is insoluble. Benzoic acid, in the form of benzoate of ammonia, is therefore, sometimes used as a means of separating peroxide of iron from some other bases. But its use requires many precautions, and it is quite inapplicable if alumina, glucina, yttria, or zirconia be present. Benzoate of silver, $Bz\,O, Ag\,O$, is sparingly soluble, and when formed in hot solutions crystallises on cooling.

2. Hyduret of Benzoyle. $C_{14}\,H_6\,O_2 = Bz\,H$.

Syn. *Essential oil of bitter almonds.* When bitter almonds, after being macerated with water for a day or two, are distilled with the water, there is obtained a fragrant oily liquid, heavier than water, which contains, besides hyduret of benzoyle, benzoic acid, hydrocyanic acid, and benzoine, a solid compound isomeric with the hyduret of benzoyle. To purify it, this oily liquid is distilled along with a mixture of protochloride of iron and slaked lime, which retain the two acids, and the benzoine remaining behind, the pure hyduret passes over.

It is a colourless transparent liquid, of a high refractive power. It has a peculiar and very powerful smell, and it is on this account that the crude oil is so much used in perfumery. Its odour has been compared to that of hydrocyanic acid, but this has arisen from the fact that the crude oil contains both; for on comparing the two, no similarity can be perceived. It ought, however, to be borne in mind that the commercial oil is highly poisonous, not only because it contains hydrocyanic acid, but because the hyduret of benzoyle is poisonous. Hyduret of benzoyle boils at 356°.

When exposed to the air, it absorbs 2 eq. of oxygen, and is converted into pure crystallised benzoic acid. $Bz\,H + O_2 = Bz\,O, H\,O$. Heated with caustic potash in close vessels, it yields benzoate of potash and hydrogen gas which is disengaged. $K\,O, H\,O + Bz\,H = K\,O, Bz\,O + H$. It is still more easily converted into benzoate of potash by an alcoholic solution of potash; the alcohol here swims above the salt, and holds in solution an oily matter not yet examined.

When hyduret of benzoyle is mixed with a little hydrocyanic acid, and placed in contact with aqua potassæ, lime water, or baryta water, it is gradually converted into the solid crystalline compound, isomeric with itself, which is called benzoine. When mixed with aqua ammoniæ, and gently heated, it produces a new compound, hydrobenzamide. With chlorine and bromine, if dry, it yields chloride and bromide of benzoyle, with hydrochloric and hydrobromic acids; if water be present, benzoic acid is likewise formed, part of which combines with some unchanged hyduret of benzoyle.

3. *Chloride of benzoyle*, formed by the action of dry chlorine on the hyduret, is a colourless liquid, of a strong disagreeable odour. It is formed as follows: $Bz\,H + Cl_2 = Bz\,Cl + H\,Cl$. With the alkalies it yields benzoate of the alkali, and chloride of the metal: $Bz\,Cl + 2\,K\,O = K\,O, Bz\,O + K\,Cl$. With dry ammonia it yields *benzamide*; with alcohol it produces benzoic ether and hydrochloric acid. $Ae\,O, H\,O + Bz\,Cl = Ae\,O, Bz\,O + H\,Cl$. When acted on by metallic bromides, iodides, sulphurets, or cyanides, it produces metallic chlorides, and bromide, iodide, sulphuret or cyanide of benzoyle. The *bromide of benzoyle* is a crystalline solid, in other respects analogous to the

chloride. The *iodide* and *sulphuret* of benzoyle are also crystallisable: the cyanide is a liquid having an odour like that of cinnamon.

4. Benzamide. $C_{14}\,N\,H_7\,O_2 = C_{14}\,H_5\,O_2 + N\,H_2 = Bz\,Ad.$

This compound is formed when dry ammonia acts on chloride of benzoyle, $Bz\,Cl + N\,H_2, H = Bz, N\,H_2 + H\,Cl$: also when hippuric acid (which see), is boiled with peroxide of lead. When prepared from the chloride, it is accompanied by sal ammoniac, formed by the hydrochloric acid produced, with the excess of ammonia. This is removed by cold water; and the benzamide, being dissolved in hot water, crystallises on cooling. It forms fine soft needles or pearly scales, very fusible and volatile. Like other amidides, it yields ammonia when boiled with alkalies, while a benzoate is formed.

5. Formobenzoilic Acid. $\left\{\begin{array}{l} C_2\,H\,O_3 + C_{14}\,H_6\,O_2 + H\,O = Fo\,O_3, \\ \quad Bz\,H + H\,O. \end{array}\right.$

This compound is obtained by adding to distilled water some crude oil of bitter almonds, which always contains hydrocyanic acid (see amygdaline), and evaporating to dryness along with some hydrochloric acid. From the dry mass, ether dissolves the new acid, which it deposits as a crystalline powder by evaporation. In this process, the hydrocyanic acid, under the influence of hydrochloric acid, is converted, along with the elements of water, into formic acid and ammonia. The latter combines with the hydrocyanic acid, the former with the hyduret of benzoile, yielding formobenzoilic acid. With bases, this acid forms salts, in which the quantity of base neutralized is exactly that which would be neutralized by the formic acid alone. Their formula is $M\,O + Fo\,O_3, Bz\,H$; by which it is seen that the hyduret of benzoyle has entered into the radical of the acid, without altering its power of saturation; and perhaps the rational formula of the acid ought rather to be, $(Fo\,O_4, Bz\,H) + H$; and that of the salts, $(Fo\,O_4, Bz\,H) + M$; which exhibits this view still more clearly.

6. Benzoate of Hyduret of Benzoyle. $C_{42}\,H_{18}\,O_8 = Bz\,O, H\,O + 2\,Bz\,H.$

This compound is formed when moist chlorine is passed through the oil of bitter almonds. Hydrated benzoic acid is formed, which unites with the unchanged hyduret. The action of moist chlorine in producing hydrated benzoic acid is as follows: $Bz\,H + 2\,H\,O + Cl_2 = 2\,H\,Cl + Bz\,O, H\,O.$ The new compound is crystalline, insoluble in water, soluble in alcohol and ether. It is volatile without decomposition. An alcoholic solution of potash dissolves it, and converts it into benzoate of potash.

7. Hippuric Acid. $C_{18}\,N\,H_8\,O_5 + H\,O$.

This acid is found in very considerable quantity in the urine of herbivorous animals, such as the horse and cow, more especially when stall-fed. It has also been lately discovered by Liebig in human urine. It is easily obtained by evaporating gently to a small bulk the fresh urine of the horse or cow, and acidulating with hydrochloric acid. On standing, the liquid deposits brown crystals of hippuric acid, which may be decolorised by a little bleaching liquor and hydrochloric acid.

The pure acid forms pretty large semi-opaque four-sided prisms, sparingly soluble in cold water, very soluble in hot water and in alcohol. When heated, it melts, and gives off benzoic acid, benzoate of ammonia, and an oily matter, which has a very fragrant odour like that of the tonka bean. By nitric acid it is converted into benzoic acid. Heated with peroxide of manganese and sulphuric acid, it yields ammonia, carbonic acid, and benzoic acid; boiled with peroxide of lead, it yields benzamide and carbonic acid.

With bases it forms salts, most of which are soluble and crystallisable.

Hippuric acid may be viewed in two ways; first, as a compound of benzamide with an acid, $C_4\,H\,O_3$ (fumaric or aconitic acid ?); secondly, as composed of hyduret of benzoyle, hydrocyanic acid, and formic acid. Either view readily accounts for its easy decomposition into benzoic acid and other products. As an ingredient of the urine, this acid is important; and we shall hereafter see that benzoic acid, taken into the system, appears in the urine as hippuric acid.

PRODUCTS OF THE DECOMPOSITION OF THE COMPOUNDS OF BENZOYLE.

1. Hyposulphobenzoic Acid. $C_{14}\,H_4\,O_3 + S_2\,O_5 + 2\,H\,O$.

A bibasic acid. Formed when anhydrous sulphuric acid acts on crystallised benzoic acid. $C_{14}\,H_5\,O_3, H\,O + 2\,S\,O_3 = C_{14}\,H_4\,O_3 + S_2\,O_5 + 2\,H\,O$. The acid is soluble and crystallisable, and forms with baryta a soluble and crystallisable salt, from which the acid may be obtained by the action of sulphuric acid. It forms two series of salts, one with 2 eq. of fixed base, the other with 1 eq. of fixed base and 1 eq. of water.

2. Bromobenzoic Acid. $C_{28}\,H_9\,Br\,O_8 + 2\,H\,O$.

A bibasic acid. When the vapour of bromine is allowed to act on benzoate of silver at the ordinary temperature, there is produced this acid, along with bromide of silver and hydrobromic acid. 2 eq. of benzoate of silver and 4 eq. of bromine yield 1 eq. bromobenzoic acid, 1 eq. hydrobromic acid, and 2 eq. bromide of silver. $2\,(C_{14}H_5O_3\,AgO) + Br_4 = C_{28}H_9\,BrO_8 + HBr + 2\,AgBr$. Ether dissolves the acid and deposits it on evaporation, in a confused mass of crystals, very sparingly soluble in water. When the acid crystallises, it takes up 2 eq. of water. With bases it forms salts, which are generally soluble and crystallisable. Their general formula is $C_{28}H_9BrO_8, 2\,MO$.

3. Benzole. $C_{12}H_6$.

SYN. *Benzine. Benzène. Phène.*—Occurs in the volatile liquids condensed from oil gas; but is best obtained in a state of purity by distilling 1 part of crystallised benzoic acid with 3 of slaked lime. It is a limpid, colourless liquid, of an agreeable etherial odour. Its Sp. G. is 0·85; it boils at 186°, and at 32° it becomes solid. It is insoluble in water, soluble in alcohol and ether. In its formation, 1 eq., of benzoic acid yields 2 eq. carbonic acid and 1 eq. benzole, the carbonic acid uniting with the lime. $C_{14}H_5O_3, HO = C_{12}H_6 + 2\,CO_2$.

4. *Sulphobenzide.* $C_{12}H_5SO_2$. When anhydrous sulphuric acid acts on benzole, a viscid mass is formed, from which, by the addition of water, is separated a new compound, which may be dissolved and crystallised by means of ether. $C_{12}H_6 + SO_3 = HO + C_{12}H_5, SO_2$. Sulphobenzide is quite neutral. 5. *Hyposulphobenzidic acid.*—This acid is found in the liquid from which the preceding compound has been deposited. Its formula is $C_{12}H_5, S_2O_5 + HO$. It may be viewed as formed by the action of 2 eq. of dry sulphuric acid on 1 eq. of benzole, $C_{12}H_6 + 2\,SO_3 = C_{12}H_5, S_2O_5, HO$; or as formed by the combination of sulphobenzide with oil of vitriol; $C_{12}H_5, SO_2 + HO, SO_3$. Either view readily explains its formation. The acid is best obtained pure from its salt with oxide of copper (which crystallises very easily), by the action of sulphuretted hydrogen. It is very soluble, and may be crystallised. It has a very acid taste, and neutralises bases, forming crystallisable salts. 6. *Nitrobenzide.* $C_{12}H_5NO_4$.—Formed when benzole is dissolved to saturation in fuming nitric acid, and water added to the hot solution. On cooling, the nitrobenzide falls to the bottom as a heavy oil. It is, at 60°, a yellow liquid, very sweet to the taste, with an odour like that of cinnamon; it boils at 434°, and solidifies at 37°. Its Sp. G. is 1·209. It is insoluble in water, soluble in alcohol and ether. It is formed from 1 eq. benzole and 1 eq. nitric acid. $C_{12}H_6 + NO_5 = HO + C_{12}H_5, NO_4$. 7. *Azobenzide.* $C_{12}H_5N$.—This compound is formed when an alcoholic solution of nitro-

benzide is distilled with dry hydrate of potash. After the alcohol has distilled, the azobenzide volatilises, forming large red crystals, fusible at 150°, boiling at 380°. The production of this compound is not yet explained; and its formula requires confirmation. 8. *Chloride of benzole.* $C_{12}H_6Cl_6$. Formed when chlorine gas and benzole are exposed to the sun's rays. It is a colourless crystalline solid. 9. *Chlorobenzine.* $C_{12}H_3Cl_3$. Obtained by distilling the preceding compound with hydrate of lime, as a colourless oily liquid.—Bromine forms with benzole analogous compounds.

10. Benzone. $C_{13}H_5O$.

One of the products of the distillation of neutral benzoate of lime. When purified from benzole and naphthaline, it is an oily viscid colourless liquid, heavier than water. It differs from 1 eq. of anhydrous benzoic acid by 1 eq. of carbonic acid. $C_{14}H_5O_3 = C_{13}H_5O + CO_2$.

11. Hydrobenzamide. $C_{42}H_{18}N_2$.

When 1 vol. hyduret of benzoyle and 20 vol. of strong aqua ammoniæ are exposed in an hermetically sealed vessel to a temperature of from 105° to 120°, it is converted after a time into a crystalline mass, which is to be washed with ether. The residue dissolved in alcohol, yields, by spontaneous evaporation, regular crystals of hydrobenzamide. In its formation, 3 eq. hyduret of benzole, and 2 eq. ammonia, produce 1 eq. hydrobenzamide and 6 eq. water. $3(C_{14}H_6O_2)+2NH_3 = C_{42}H_{18}N_2 + 6HO$. If, in preparing this substance, we employ the crude oil of bitter almonds, we obtain a yellow resinous mass, which is a mixture of *hydrobenzamide, benzhydramide, azobenzoyle,* and *azotide of benzoyle,* all of them discovered by Laurent. 12. *Benzhydramide* is isomeric with hydrobenzamide, but is not converted, like the former, into hyduret of benzoyle and sal-ammoniac by the action of hydrochloric acid. 13. *Azobenzoyle.* $C_{42}H_{15}N_2$, is much less soluble in alcohol than the preceding. It is derived from benzoyle as follows:—$3(C_{14}H_5O_2) + 2NH_3 = C_{42}H_{15}N_2 + 6HO$. 14. *Azotide of benzoyle,* $C_{14}H_5N$, is quite insoluble in boiling alcohol. It may be derived from anhydrous benzoic acid as follows; $C_{14}H_5O_3 + NH_3 = C_{14}H_5N + 3HO$.

15. Benzimide. $C_{28}NH_{11}O_4$.

According to Laurent, this compound is found in the crude oil of bitter almonds. It is crystallisable, and appears to be decomposed by acids into benzoic acid and ammonia. It may be derived from anhydrous bibenzoate of ammonia by the separation of 2 eq. water. $C_{28}H_{10}O_6 + NH_3 = C_{28}H_{11}NO_4 + 2\,HO$. But this is not probable. A compound precisely similar is obtained when an alcoholic solution of potash is added to a mixture of hyduret of benzoyle and strong hydrocyanic acid; but this compound yields with acids ammonia and hyduret of benzoyle.

16. Benzoine. $C_{14}H_6O_2$.

Isomeric with hyduret of benzoyle. It is formed when an alcoholic solution of potash, or sulphuret or cyanide of potassium, act on the crude oil of bitter almonds, containing hydrocyanic acid. It separates in a congeries of small crystals, insoluble in water, soluble in alcohol. It may be volatilised without change. Sulphuric acid dissolves it with a violet colour. Hydrate of potash, melted with it, forms benzoate of potash, with disengagement of hydrogen. It dissolves with a violet colour in a hot alcoholic solution of potash, and is converted by boiling with it into benzilic acid. When its vapour is passed through a red-hot tube, it is converted into hyduret of benzoyle, or at least into an oil smelling like that compound, and passing into benzoic acid on exposure to the air. By the action of chlorine it loses hydrogen, and is converted into *Benzile*, a compound having the composition of the radical benzoyle.

The action of hydrocyanic acid in promoting the formation of benzoine is not yet explained; but it is certain that from pure hyduret of benzoyle we cannot procure it, while the addition of hydrocyanic acid ensures its formation.

17. Hydrobenzoinamide.

SYN. *Benzoniamide.*—Isomeric with hydrobenzamide. It is formed by exposing a mixture of benzoine and ammonia to a moderate heat; and appears as a white tasteless powder, volatile without decomposition.

18. Benzile. $C_{14}H_5O_2$.

SYN.—*Benzoyle.* It is formed by the action of chlorine gas on melted benzoine. When cold the mass is boiled with alcohol, which on cooling deposits benzile in crystals which are yellow six-sided prisms; insoluble in water, soluble in alcohol and ether, melting at 195° and volatile without decomposition. An alcoholic solution of potash dissolves it with a violet colour, and converts it into benzilic acid.

19. Benzilic Acid. $C_{28}H_{11}O_5 + HO$.

Formed when benzile is dissolved in a hot alcoholic solution of potash, and boiled until the violet colour at first produced has disappeared, and is no longer restored by a fresh portion of potash. To the boiling solution of benzilate of potash hydrochloric acid is added in excess, and on cooling the benzilic acid is deposited in colourless brilliant crystals, fusible at 248°, not volatile, but yielding, when heated, benzoic acid, and purple vapours. Sulphuric acid dissolves it with a bright crimson colour. Its formation is explained as follows:—2 eq. of benzile take up 2 eq. of water, one of which is incorporated in the acid; while the other is replaceable by bases. $2\,(C_{14}\,H_5\,O_2)+2\,HO = C_{28}\,H_{11}\,O_5+HO$. *Benzilate of potash* forms large transparent crystals, soluble in water and alcohol.

20. *Azobenzoide.*—$C_{84}\,H_{33}\,N_5$? Obtained by adding ammonia to the oil produced when bitter almonds are distilled per descensum, and dissolving away by means of ether all other products. A white powder, decomposed by heat. Its formula is doubtful.

21. *Cyanobenzile.*—Formed when an alcoholic solution of benzile is warmed with $\frac{1}{3}$ of its volume of concentrated hydrocyanic acid. It is deposited in large transparent crystals, the composition of which is not yet known.

21. Hyduret of Sulphobenzoyle. $C_{14}\,H_5\,S_2,\ H$.

One vol. of crude essence of bitter almonds is dissolved in 8 or 10 of alcohol, and gradually mixed with 1 vol. of hydrosulphuret of ammonia. After a time, the mixture deposits a fine white powder, formed of grains smaller than those of starch, which give to the fingers a very persistent odour of garlic. It is insoluble in water and alcohol. Ether liquefies it, but a few drops of alcohol restore its solid form. It may be considered as the hyduret of a new radical, in which the oxygen of benzoyle has been replaced by sulphur. When heated, it melts, and if now allowed to cool, forms first a transparent plastic mass, and afterwards a brittle glass. If kept melted for some time, it crystallises, but is now altered.

22. Stilbene. $C_{28}\,H_{12}$.

When the preceding compound is strongly heated, it gives off a large quantity of sulphuretted hydrogen, and a little of a liquid, apparently bisulphuret of carbon. Continuing the heat, there distil over, first a substance crystallising in pearly scales, *stilbene;* and later, a compound crystallising in needles, called by Laurent, the discoverer, *sulphessale.* To obtain the stilbene pure, the first crystals are dissolved in boiling alcohol, which leaves undissolved the other body, and on cooling deposits stilbene in tables. These being dissolved in hot ether, form, by slow evaporation, remarkably fine crystals, with the pearly lustre of stilbite, hence the name. It is fusible and volatile, and combines with chlorine and bromine. Nitric acid decomposes it, giving rise to several new products. Strong chromic acid attacks it with violence, and reproduces hyduret of benzoyle.

Chloride of stilbene is formed when chlorine is passed through melted stilbene. It appears in two isomeric modifications, *a* and *b*, both of which have the formula $C_{28}\,H_{12},\ Cl_2,$ but crystallise in different forms. By the action of a boiling alcoholic solution of potash, each loses 1 eq. of hydrochloric acid (or its elements), and thus they produce two isomeric modifications of a new compound $C_{28}\left\{\begin{matrix}H_{11}\\ Cl,\end{matrix}\right.$ which Laurent calls Chlostilbase; and in which 1 eq. of hydrogen of stilbene is replaced by chlorine. One of these is called Chlostilbase *a*, the other Chlostilbase *b*. Both are oily liquids, but they are distinguished by the action of bromine, which combines with both, producing again two isomeric compounds, both crystallisable, but in entirely different forms. Their formulæ are, *a* $C_{28}\left\{\begin{matrix}H_{11}\\ Cl\end{matrix}\right. + Br_2$ and *b* $C_{28}\left\{\begin{matrix}H_{11}\\ Cl\end{matrix}\right. + Br_2$.

Along with chloride of stilbene is formed another compound, chloride of chlostilbase, analogous to these bromides of chlostilbase. It is a crystallisable solid: formula, $C_{28}\left\{\begin{matrix}H_{11}\\ Cl\end{matrix}\right. + Cl_2$.

Bromide combines with stilbene, forming the bromide of stilbene, $C_{28}\,H_{12},\ Br_2,$ which is a white powder.

When stilbene is boiled with nitric acid, it forms several compounds not yet fully examained. Among these are Nitrostilbase, Nitrostilbèse, and Nitrostilbic acid. The latter, according to Laurent, is $C_{28}\,H_{11}\,N\,O_{14}$.

23. *Hyduret of Sulphazobenzoyle*, $(C_{14}\,H_5\,S_{\frac{4}{3}}\,N_{\frac{2}{3}})\,H$, is generally formed along with hyduret of sulphobenzoyle. It seems to be hyduret of benzoyle, in which the 2 eq. oxygen of the benzoyle are replaced partly by sulphur, partly by nitrogen. Besides these compounds, Laurent has described a hydrosulphuret of azobenzoyle, with the strange formula $C_{14}\,H_6\,SN_{\frac{3}{4}}$. Ought it not rather to be $C_{14}\,H_6\,S\,N$?

By the action of ammonia on the crude essence, he has obtained two other compounds, *Azobenzoidine*, $C_{14}\,H_6\,N_{\frac{5}{3}}$ (?); and *Azobenzoilide*, isomeric with it; also two which he calls *hyduret of azobenzoyline* and *hyduret of benzoyline*, the former $C_{14}\,H_6\,N_{\frac{4}{3}}$: the latter isomeric with the crude essence.

All these compounds are interesting, but the most recent researches of Laurent go to prove that the formula of the last-named compound should be trebled, $C_{42}\,H_{18}\,N_{5}$, and that it is a base, which he calls *amarine.*

24. Nitrobenzoic Acid. $C_{14}\,H_{4}\,N\,O_{7}, H\,O$.

Formed when nitric acid acts on benzoic acid. It is a crystalline volatile acid, and contains the elements of benzoic acid, in which 1 eq. hyponitric or nitrous acid has been substituted for 1 eq. hydrogen. $C_{14}\,H_{5}\,O_{3}-H+NO_{4}=C_{14}\left\{\begin{matrix}H_{4}\\NO_{4}\end{matrix}\right.O_{3}$; and the basic water of the benzoic acid unites with the new acid as with the old.

25. Bromide of Benzole. $C_{12}\,H_{6}, Br_{6}$.

This compound is formed as a white insoluble powder, when bromine acts on benzole. An alcoholic solution of potash removes hydrobromic acid (or its elements), and causes the separation of a white crystalline body, $C_{12}\left\{\begin{matrix}H_{3}\\Br_{3}\end{matrix}\right.$, which Laurent calls *bromobenzinise;* and which is formed by substitution of bromine for half the hydrogen of benzole. The bromide of benzole may, therefore, be $C_{12}\left\{\begin{matrix}H_{3}\\Br_{3}\end{matrix}\right.+3\,HBr$.

26. *Hydrocyanate of benzoine.* $C_{46}\,N_{2}\,H_{18}\,O_{4}$, is formed as a light crystalline matter, when oil of bitter almonds is mixed with one-fourth its volume of dry hydrocyanic acid, and warmed with its own volume of aqua potassæ, Sp. G. 1·25, diluted with six parts of alcohol. It arises from the action of 3 eq. hyduret of benzoyle and 2 eq. hydrocyanic acid: $3\,(C_{14}\,H_{6}\,O_{2})+2\,(C_{2}\,NH)=C_{46}\,N_{2}\,H_{18}\,O_{4}+2\,HO$.

27. *Hydrocyanate of benzile,* $C_{14}\,H_{5}\,O_{2}+C_{2}\,NH=C_{16}\,NH_{6}\,O_{2}$, is formed by direct combination when a hot alcoholic solution of benzile is mixed with an equal bulk of anhydrous hydrocyanic acid. It forms large colourless crystals.

Appendix to Benzoyle.

1. Amygdaline. $C_{40}\,NH_{27}\,O_{22}$.

Is found in bitter almonds, in the leaves of the cherry laurel, and probably in the kernels of all the bitter species of amygdalus and prunus, as the peach and plum. To obtain it, bitter almonds are pounded and forcibly pressed between warm iron plates to remove the fat oil (oil of almonds). The marc or residue is boiled with alcohol of 94 per cent., and the tinctures distilled off in the water-bath to the consistence of syrup. This liquid, which contains amygdaline and sugar, is diluted with water, mixed with yeast, and set aside. When the fermentation is over, the whole is filtered, and again evaporated to a syrup, which being mixed with a large excess of cold alcohol (of 94 per cent.) deposits the amygdaline as a white crystalline powder. This is pressed in folds of bibulous paper, and finally purified by repeated crystallisation from boiling alcohol. It forms crystalline scales, very soluble in water, very sparingly soluble in cold alcohol, but more soluble in hot alcohol. It has a bitter taste. When heated it emits an odour like that of May blossom, and leaves a bulky coal.

When distilled with nitric acid, or other oxidising agents, it is resolved into ammonia, hyduret of benzoyle, benzoic acid, formic acid, and carbonic acid. Caustic alkalies convert it into ammonia and amygdalinic acid: permanganate of potash converts it into cyanate and benzoate of potash.

2. Amygdalinic Acid. $C_{40} H_{26} O_{24} + HO$.

Prepared by boiling amygdaline with baryta as long as ammonia is given off, and then removing the baryta from the soluble amygdalinate of that base by sulphuric acid. By evaporation it yields a transparent amorphous mass, which has a very pleasant acid taste. Nitric acid, and other oxidising agents, convert it into hyduret of benzoyle, with formic and benzoic acid. Its salts are almost all soluble: their formula is $C_{40} H_{26} O_{24} + MO$.

3. Distilled Water of Bitter Almonds.

Expressed bitter almonds are made into a thin cream with water, and this distilled in the heat of a chloride of calcium bath, till a quantity of water has passed over equal in weight to the almonds before being pressed. The distilled water is milky from suspended oil of bitter almonds, and smells both of hyduret of benzoyle and of hydrocyanic acid. When freshly prepared, it contains little more than 1 grain of hydrocyanic acid per ounce; but its strength diminishes by keeping, and as it is difficult to obtain it of uniform strength even when fresh, it is not a good form of administering hydrocyanic acid. It is remarkable, that nitrate of silver does not detect the hydrocyanic acid, unless ammonia is added with the nitrate, and after a time neutralised by nitric acid. It is used in medicine, especially on the Continent, and is poisonous.

4. Laurel Water.

Obtained by distilling two parts of fresh leaves of *prunus laurocerasus* with water till three parts have passed over. It exactly resembles the preceding water, and is equally uncertain, and equally poisonous.

THEORY OF THE FORMATION OF HYDURET OF BENZOYLE FROM BITTER ALMONDS.

Bitter almonds contain, like sweet almonds, a large quantity of an albuminous or caseous matter, called *emulsine* or *synaptase*, along with abundance of a mild fat oil, the oil of almonds, very similar to olive oil. But in addition to these, the bitter almonds contain 4 or 5 per cent. of amygdaline, which is not present in sweet almonds.

Now, if the amygdaline be removed by boiling alcohol, the residue, when distilled with water, does not yield a trace of the volatile oil of bitter almonds. Again, if the residue of the bitter almonds, after the fat oil has been pressed out, be heated to such a point as to coagulate the emulsine, before water is added, the distillation also yields no volatile oil, even although the amygdaline be present.

These facts prove that the production of the volatile oil of bitter almonds depends on the presence, first, of amygdaline, secondly of soluble emulsine ; and that is the result of the mutual action of these bodies on each other. This is further demonstrated by the fact that if amygdaline be placed in contact with the emulsine or synaptase of *sweet almonds*, and water, distillation of the mixture now yields the oil abundantly.

When the solution of 10 parts of amygdaline in 100 of water is added to a solution of 1 part of synaptase in 10 of water, mutual decomposition at once takes place : the liquid acquires the odour of hyduret of benzoyle and of hydrocyanic acid, and when distilled, yields the crude oil of bitter almonds, which is a mixture of these two compounds. The residue of the distillation contains sugar in such quantity, that it is probable the elements of the synaptase have contributed to form it ; and when this sugar is destroyed by fermentation, a fixed acid is found. If the synaptase has been coagulated, it has not the slightest action on amygdaline.

When the expressed bitter almonds are moistened with water, the very same reaction occurs ; and if enough water be present to dissolve the oil as it is formed, the whole amygdaline disappears in a short time. But if the expressed almonds be thrown into boiling water, the synaptase coagulates, and can then produce no change in the amygdaline. To obtain the full proportion of oil, 1 part of expressed almonds should be macerated for 24 hours with 20 parts of water at about 102°, and then distilled.

100 parts of amygdaline produce 47 of crude oil, and these 47 parts of crude oil contain almost exactly 6 of anhydrous hydrocyanic acid ; so that 17 grains of amygdaline, dissolved in 1 oz.

of emulsion of *sweet* almonds, yields a mixture containing 1 grain of dry hydrocyanic acid, and consequently of the same strength as the distilled water professes to be. This mixture has, besides, the advantage of containing the hyduret of benzoyle present in the distilled water, to which is perhaps owing the superiority of the distilled water of bitter almonds on laurel leaves over mere diluted hydrocyanic acid, a superiority which, according to the Continental physicians, is very decided and obvious. The above simple recipe, given by Liebig and Wöhler, is admirably adapted for extemporaneous use, and the mixture ought never to be made in larger quantity at a time, as, like the distilled water, it alters by keeping.

In the above remarkable decomposition, we have a very beautiful example of a metamorphosis in which the elements of two bodies take a share; but as the whole of the products are not yet exactly known, and even the composition of the emulsine or synaptase is uncertain, we cannot explain the whole change with precision. We know, however, that from 1 eq. amygdaline, $C_{40}NH_{27}O_{22}$, the following compounds may be derived :—

1 eq. hydrocyanic acid	C_2	N	H	
2 eq. hyduret of benzoyle	C_{28}		H_{12}	O_4
½ eq. sugar	C_6		H_5	O_5
2 eq. formic acid	C_4		H_2	O_6
7 eq. water			H_7	O_7
1 eq. amygdaline	C_{40}	N	H_{27}	O_{22}

Also, 1 eq. amygdalinic acid, $C_{40}H_{26}O_{24}$, may yield

3 eq. formic acid	C_6	H_3	O_9
2 eq. hyduret of benzoyle	C_{28}	H_{12}	O_4
½ eq. sugar	C_6	H_5	O_5
6 eq. water		H_6	O_6
1 eq. amygdalinic acid	C_{40}	H_{26}	O_{24}

Now, we can trace all these products among the results of this transformation ; and it is probable, not only that there is more sugar than can be accounted for by the amygdaline, but also that other products, not yet known, are formed : as, for example, the fixed acid above alluded to. The emulsine or synaptase, which produces this remarkable change in amygdaline, in which it itself participates, contains nitrogen, is soluble in water, coagulable by heat, and in short very analogous both to albumen and caseine, along with which we shall again notice it. In the almond it appears to be accompanied by albumen.

We have seen, above, that the assumption of the existence of the radical benzoyle brings a number of compounds into a more easily understood form, and very materially aids the memory by enabling us to classify these compounds as analogous to others better known. Other views may be taken of this series of compounds: for example, according to Dumas, hyduret of benzoyle may be represented as a compound of benzoic acid with a carbo-hydrogen: $2\,C_{14}H_5O_3 + (C_{14}H_5)\,H_3$: benzoic acid being the teroxide and the carbo-hydrogen the terhyduret of the body, $C_{14}H_5$: for $2\,(C_{14}H_5)\,O_3 + (C_{14}H_5)\,H_3 = C_{42}H_{18}O_6 = 3\,(C_{14}H_6O_2) = 3\,BzH$. The same view might be extended to some of the other compounds of benzoyle, but it is complex, and cannot well be applied to benzamide, hydrobenzamide, and several others. Again, according to Mitscherlich, benzoic acid is $C_{12}H_6 + 2\,CO_2$; that is, benzole plus 2 eq. carbonic acid; while a dry benzoate would contain, united to the base, the hypothetical body *benzide*, $C_{12}H_5$, and the equally hypothetical anhydrous oxalic acid, C_2O_3. These views appear both to be in all respects inferior to that which we have adopted, and which must be retained, until a better shall be proposed.

XIV. SALICYLE. $C_{14}H_5O_4 = Sa$.

This is the hypothetical radical of a remarkable series of compounds; and, as such, belongs to the same group as benzoyle. Its most interesting compound is the hyduret of salicyle, which we shall therefore first consider.

1. Hyduret of Salicyle. $C_{14}H_5O_4, H = Sa\,H$.

Syn. Salicylous acid. This compound is found as the chief ingredient in the essence of meadowsweet, that is, the essential oil obtained by distilling the flowers of *spiræa ulmaria* with water. It is probable that, like the essence of bitter almonds, it is formed by the metamorphosis of a compound or compounds present in the flowers. The crude essence is distilled with aqua potassæ, which combines with the hyduret, and an oil distils over which seems to be a carbo-hydrogen. The salt of potash being now redistilled with a slight excess of dilute sulphuric acid, yields the pure hyduret of salicyle.

It may also be obtained by distilling one part of salicine, one part of bichromate of potash, two and a half of oil of vitriol, and twenty of water, together. The salicine is dissolved in part of the water, and the acid diluted with the rest. The mixture is then made in a retort, and after the effervescence which takes place is over, the whole is distilled, and yields the hyduret, to the amount of one-fourth of the salicine employed.

Hyduret of salicyle is an oily colourless liquid having a fragrant aromatic odour, and a burning taste. Its Sp. G. is 1·1731, and it boils about 380°. With chlorine and bromine it forms new compounds. With bases it forms salicylurets, water being separated. $H\,Sa + M\,O = H\,O + M\,Sa$, so that it has the characters of an acid.

Salicyluret of ammonium. $Sa, N\,H_4$, is formed when concentrated ammonia is poured upon hyduret of salicyle. It is a yellow solid, having a faint odonr of roses. When moist, this salt is decomposed spontaneously, becoming black, and giving off ammonia and an odour like that of roses. With dry ammoniacal gas, hyduret of salicyle forms the compound $3\,Sa\,H + 2\,N\,H_3$.

Salicylimide, $C_{42}N_2H_{18}O_6$, is formed when caustic ammonia is added, drop by drop, to a solution of 1 vol. hyduret of salicyle in 3 vol. alcohol, and the small yellow crystals which first formed are dissolved by a gentle heat. On standing, salicylimide appears in the form of golden yellow brilliant prisms. It is formed from 3 eq. hyduret of salicyle and 2 eq. of ammonia, by the separation of 6 eq. water, $3\,(C_{14}H_6O_4) + 2\,N\,H_3 - 6\,H\,O = C_{42}N_2H_{18}O_6$. As it is no longer soluble in the liquid from which it was first deposited, it is probable that the yellow salt first formed, which dissolved in the alcohol by aid of a gentle heat, was salicyluret of ammonium, which by excess of ammonia, was converted into salicylimide.

The salts of the hyduret of salicyle or hydrosalicylic acid, are constituted, for the most part, according to the formula $Sa\,M$. The potassium salt, $Sa\,K$, when exposed to the air in a moist state, becomes first green, then black. When the change is complete, water dissolves acetate of potash, and leaves a black matter, ***melanic acid,*** $C_{10}H_4O_5$: 1 eq. of salicyluret of potassium, 2 eq. water, and 3 eq. oxygen, contain the elements of 1 eq. acetate of potash, and 1 eq. melanic acid, $C_{14}H_5O_4, K + 2\,H\,O + O_3 = C_4H_3O_4, K + C_{10}H_4O_5$. Melanic acid combines with bases.

2. Salicylic Acid. $(C_{14}\,H_5\,O_4)\,O, H\,O = SaO, HO = Sa\,O_2\,H$.

Formed when hyduret of salicyle is heated with hydrate of potash till the mass loses its brown colour. Hydrogen is given off, and salicylate of potash is formed. Hydrochloric acid, added to the solution of this salt, causes the deposition of crystals of salicylic acid.

The same acid is formed when coumarine, the stearoptene or camphor of the tonka bean, is acted on by caustic potash. Moreover the essential oil of winter-green, or *Gaultheria procumbens,* appears, by the researches of Cahours and Gerhard, to be the salicylate of oxyde of methyle.

Salicylic acid crystallises in tufts of slender prisms, very like benzoic acid. It may be sublimed without decomposition. The formation of this acid from hyduret of salicyle is very simple: $C_{14}H_5O_4, H + KO, HO = C_{14}H_5O_5, KO + H_2$. When the salicylate of potash is decomposed by an acid, the salicylic acid takes up 1 eq. of basic water, and separates as $C_{14}H_5O_5, HO$, or $C_{14}H_5O_6, H$. The decompositions of this acid are very interesting, connecting it with several other series of organic compounds.

When it is acted on by nitric acid, it is first converted into indigotic acid, or anilic acid, $C_{14}H_4NO_9, HO$, along with other products; and by the continued action of nitric acid, there is finally produced the remarkably bitter acid, called carbazotic, or nitropicric acid, $C_{12}H_2N_3O_{13}, HO$. Both these acids are formed from indigo by the action of nitric acid.

When salicylic acid is distilled with caustic baryta, it yields carbonate of baryta, and a heavy oily liquid, which is the acid known as carbolic acid (Runge), and hydrate of phenyle (Laurent), the formula of which is $C_{12}H_6O_2 = C_{12}H_5, O, HO$. The production of carbolic acid from sailcylic acid is easily understood: it is in fact analogous to that of benzine from benzoic acid. $C_{14}H_5O_5, HO + 2BaO = 2(BaO, CO_2) + C_{12}H_6O_2$. As the action with baryta is so violent as to destroy a goeat part of the acid, it is found better to heat rapidly salicylic acid mixed with powdered glass, when it is resolved into carbolic and carbonic acids.

Now it is very remarkable, that carbolic acid, which is one of the chief ingredients of the oil of coal tar, a product, therefore, of the destructive distillation, is also converted by the action of nitric acid into nitropicric acid. This would indicate that when salicylic acid is acted on by nitric acid, it yields, first, some compound containing the same radical as carbolic and nitropicric acid, and that this is further oxidised into the latter acid. We shall hereafter see that the probable radical of carbolic acid is *phêne*, $C_{12}O_6$, from which, by substitution and oxidation, carbolic and nitropicric acids, and a whole series of compounds, may be formed.

On the whole, from its relation to hyduret of salicyle and to salicine (from which it may also be formed by the action of caustic potash), from its analogy in formation, constitution, and properties to benzoic acid, from its occurrence in nature in the first compound of methyle not artificially produced, and from its ready convertibility into indigotic acid, carbolic acid, and nitropicric acid, salicylic acid is a compound of very great interest.

The salts of salicylic acid have the general formula $C_{14}H_5O_5$, M O or $C_{14}H_5O_6$, M. The salicylate of oxide of methyle C_2O_3, $O + C_{14}H_5O_5$, occurs in the essential oil of *Gaultheria procumbens,* and is much used in perfumery. It gives rise to a number of remarkable products, when subjected to the action of nitric acid, chlorine, bromine, alkalies, &c.; but all these things will be treated of in their proper places.

3. Chlorosalicylic Acid. $C_{14}H_5\left\{\begin{matrix}O_4\\Cl\end{matrix}\right.$ or $C_{14}H_5O_4$, Cl.

When dry chlorine is made to act on dry hyduret of salicyle, this compound is formed, along with hydrochloric acid; it crystallises readily, and may be sublimed unchanged. Its formation is entirely analogous to that of chloride of benzoyle, and it might be viewed as chloride of salicyle, $C_{14}H_5O_4, Cl = Sa\,Cl$. But its properties are those of an acid, and hence we are compelled to consider it as salicylic acid, $C_{14}H_5O_5$, in which 1 eq. oxygen has been replaced by 1 eq. chlorine, the type remaining unchanged. Hence, after this substitution, it is still an acid, and its true formula is $C_{14}H_5\left\{\begin{matrix}O_4\\Cl\end{matrix}\right.$ an acid of the type of anhydrous salicylic acid.

With ammonia it forms a new compound, *chlorosalicylimide.* As in the action of ammonia on hyduret of salicyle, so in this case, 2 eq. ammonia act on 3 of the acid, and 6 of water are separated. The formula of chlorosalicylimide, which is a yellow, insoluble solid, is $C_{42}H_{15}N_2Cl_3O_6$; for $3(C_{14}H_5Cl\,O_4) + 2\,NH_3 = 6\,HO + C_{42}H_{15}Cl_3N_2O_6$. It is, in fact, salicylimide in which 3 eq. chlorine have been substituted for 3 eq. hydrogen.

With bromine and iodine, hyduret of salicyle yields the two analogous compounds, bromosalicylic acid, and iodosalicylic acid; $C_{14}H_5\left\{\begin{matrix}O_4\\Br\end{matrix}\right.$ and $C_{14}H_5\left\{\begin{matrix}O_4\\I\end{matrix}\right.$.

4. Nitrosalicylic Acid, $C_{14}H_5NO_8$*$=C_{14}H_5\left\{\begin{matrix}O_4\\NO_4\end{matrix}\right.$.

This acid is formed by the action of nitric acid on hyduret of salicyle. It forms yellow prisms, and with bases, yields yellow detonating salts. Ammonia colours it blood-red, and perchloride of iron cherry-red. It would appear, according to the above formula, derived from the analysis of Piria, to be salicylic acid, in which 1 eq. nitrous (hyponitric) acid is substituted for I eq. oxygen. But its characters, and those of its salts, are such as to lead to the suspicion that it is identical with the nitrophenesic acid of Laurent (derived from carbolic acid by the action of nitric acid), the formula of which is $C_{12} H_3 N_2 O_9, HO$. The subject requires further investigation. It is not improbable that this acid may ultimately be found identical with indigotic acid, $C_{14} H_4 NO_9, HO$.

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* In the 7th edition of Turner's Chemistry, on the authority of Liebig, (see his edition of Geiger's Handbuch, p. 689) the formula $C_{12}H_3N_4O_{12}$ is given for this acid. The formula in the text is given as that of Piria in the French edition of Liebig's Organic Chemistry, published about the same time or later. I suspect some error of the press in the latter. The formula given in Turner approaches very nearly to that of nitrophenesic acid.—W. G.

APPENDIX TO SALICYLE.

5. Salicine. $C_{42} H_{29} O_{22} = C_{42} H_{23} O_{16} + 6 HO$.

This compound occurs in the bark of all such willows as are bitter, such as *Salix helix, S. amygdalina*, &c. It is extracted by boiling with water, decolorising the decoction with litharge, removing the lead dissolved by sulphuric acid and sulphuret of barium, and evaporating to a syrup. The salicine crystallises on standing, in fine scales of a silky lustre, which have a very pure bitter taste, and are highly febrifuge. It is neutral, soluble in water and alcohol, insoluble in ether. Oil of vitriol colours it blood-red. When a mixture of acetate of lead with ammonia is added to a solution of salicine, there is formed a precipitate, which appears to be $C_{42} H_{23} O_{16} + 6 PbO$. Distilled with bichromate of potash and sulphuric acid, it yields formic and carbonic acids, hyduret of salicyle, and a resinous matter.

Saliretine. $C_{30} H_{15} O_7 + HO$. When salicine is boiled with diluted sulphuric or hydrochloric acid, it deposits a yellowish white powder, which has the characters of a resin. This is saliretine. It is insoluble in water and ammonia, soluble in alcohol. Oil of vitriol colours it blood-red; heated with nitric acid, it yields nitropicric acid. Its formation is accompanied by the production or separation of grape sugar. In fact, salicine, plus 1 eq. hydrogen, contains the elements of saliretine and of grape sugar. $C_{42} H_{29} O_{22} + H = C_{30} H_{15} O_7, HO + C_{12} H_{14} O_{14}$.*

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* In the 7th edition of Turner's Chemistry, it is erroneously stated, at p. 815, that salicine alone contains the elements of saliretine and of grape sugar. The error is obvious in the equation, $C_{30} H_{16} O_8 + C_{12} H_{14} O_{14} = C_{42} H_{29} O_{22}$; where H_{29} should be H_{30}: but salicine contains only H_{29}. Qu.? Is not saliretine $C_{30} H_{14} O_7 + HO ? = C_{30} H_{15} O_8$? If so, the eq. of hydrogen in the text would not be required.—W. G.

Chlorosalicine. When chlorine is made to act on a solution of salicine, there is obtained a powder, $C_{42} H_{25} Cl_4 O_{22}$. This is chlorosalicine, which is salicine, having 4 eq. of chlorine substituted for 4 eq. hydrogen. If heat be applied during the operation, a red liquid is formed, which is $C_{42} H_{18} Cl_7 O_{18}$. It appears to be formed from salicine, *minus* 4 eq. water, $C_{42} H_{25} O_{18}$, by the substitution of 7 eq. chlorine for 7 eq. hydrogen.

Rutiline is the name given to the red compound formed by the action of oil of vitriol on salicine. When pure it is of a deep reddish-brown colour: acids change it to a bright red, alkalies to a deep violet.

6. Phloridzine. $C_{42} H_{29} O_{24} = C_{42} H_{23} O_{18} + 6 HO$.

This is a substance, very analogous to salicine, which occurs in the bark of the roots of the apple, pear, plum, &c. It is extracted in the same way as salicine, and resembles it much; forming small scales, soluble in hot water, and in alcohol, very bitter, and powerfully febrifuge. It may be viewed as salicine, *plus* 2 eq. oxygen, or as a higher oxide of the same radical. When boiled with dilute sulphuric acid, it yields a resinous compound, *phloretine*, analogous to saliretine, along with grape sugar. Phloretine is $C_{30} H_{15} O_{10} = C_{30} N_{14} O_9, HO$; and $C_{30} H_{15} O_{10} + C_{12} H_{14} O_{14} = C_{42} H_{29} O_{24}$. According to Stas, however, Phloretine is $C_6 H_3 O_2$, or double or quadruple of this. The compound of phloretine with oxide of lead he found to be $C_{12} H_5 O_3, 2 Pb O$; which would indicate, for hydrated phloretine, $C_{12} H_5 O_3, 2 HO = C_{12} H_6 O_4, HO = C_{12} H_7 O_5$.

By the action of nitric acid on phloridzine, there is formed a puce-coloured acid, nitrophloretic acid, which, according to Piria, is $C_{30} H_{12} NO_{15}$; according to Stas, $C_{24} H_{10} NO_{12}$.

Phloridzéine. $C_{42} H_{29} N_2 O_{26}$. When moist phloridzine is exposed to air and ammonia, it is transformed into a deep red compound, which dissolves in ammonia, and may be precipitated by acids. It is equal to phloridzine, *plus* 8 eq. oxygen and 2 eq. ammonia. When dissolved in ammonia, and dried in vacuo, it leaves a purple mass, with coppery lustre, which communicates to water a splendid blue colour. This is a compound of phloridzéine and 1 eq. ammonia. The formation of this blue pigment is a very good example of that kind of eremacausis with the aid of ammonia, by which indigo, litmus, orchil, &c. are produced from colourless bodies.

XV. Cinnamyle. $C_{18} H_8 O_2 = Ci$.

The radical of essence of cinnamon, but unknown in a separate form.

1. Hyduret of Cinnamyle. $Ci\,H = C_{18}\,H_8\,O_2, H.$

This is the purified essence, or oil of cinnamon. The oil of commerce contains, besides, cinnamic acid and two resins, all of which have been produced from the original oil, $C_{20}\,H_{11}\,O_2$ by the additions to 3 eq. of it, of 8 eq. oxygen. $3\,(C_{20}\,H_{11}\,O_2) + O_8 = C_{18}\,H_8\,O_4$ (cinnamic acid) $+ C_{12}\,H_5\,O$ (a resin); $+ C_{30}\,H_{15}\,O_4$ (another resin), $+ 5\,HO$. With less oxygen, hyduret of cinnamyle, $C_{18}\,H_8\,O_2$, is formed, along with the resins, so that the oil of commerce contains, besides the original oil, all the compounds above mentioned.

The hyduret of cinnamyle, Ci H, is a fragrant oil. It forms, with nitric acid, a crystalline compound, $Ci\,H + NO_5$, which, when mixed with water is resolved into its constituents, hyduret of cinnamyle and nitric acid. When the hyduret is exposed to the air, it absorbs oxygen, producing cinnamic acid, $Ci\,O, HO = C_{18}\,H_8\,O_3, HO$.

The fresh oil of cinnamon is, as has been stated, $C_{20}\,H_{11}\,O_2$. With 6 eq. oxygen from the air, it yields hyduret of cinnamyle and the two resins: with 2 eq. more, the hyduret passes into cinnamic acid. With oil of vitriol, 3 eq. of the fresh oil $= C_{60}\,H_{33}\,O_6$, lose 3 eq. water, and form two resins, one $= C_{30}\,H_{15}\,O$; the other $= C_{30}\,H_{15}\,O_2$. With hydrochloric acid, it yields an oil and two resins; one, $C_{20}\,H_8\,O$; the other $C_{14}\,H_6\,O$.

2. Cinnamic Acid. $C_{18}\,H_7\,O_3 + HO = Ci\,O, HO.$

Formed by exposing oil of cinnamon to the air. It is most easily obtained by dissolving the oil of balsam of Peru in an alcoholic solution of potash, evaporating to dryness, dissolving in hot water, and adding to the solution of cinnamate of potash an excess of hydrochloric acid. It crystallises very readily, and may be sublimed. By the action of nitric acid, cinnamic acid is converted into hyduret of benzoyle, and into an acid very similar to benzoic acid, if not identical with it. When cinnamic acid is added to cold nitric acid, it forms an acid, $C_{18}\,H_7\,NO_8 = C_{18}\,H_8\,O_4 - H + NO_4$; that is, cinnamic acid, in which 1 eq. of nitrous acid is substituted for 1 of hydrogen; $C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right.O_3, HO$. This is *nitrocinnamic acid.* Its salts detonate when heated. With oxide of ethyle, it forms a crystallisable ether, $Ae\,O, C_{18}\,H_6\,NO_7$.

When oil of cinnamon is acted on by nitric acid with the aid of heat, it yields benzoic and nitrobenzoic acids. By the action of chlorine, oil of cinnamon is converted into several new products, one of which is *chlorocinnose,* $C_{18}\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right.O_2$. It is hyduret of cinnamyle in which 4 eq. of chlorine are substituted for 4 eq. of hydrogen.

Balsam of Peru contains compounds connected with cinnamyle. The principal is an oil, *cinnameine,* which, when boiled with alkalies, yields cinnamic acid and a neutral oily body, *peruvine,* $C_{18} H_{12} O_2$. Cinnamine, heated with dry potash, yields hydrogen gas and pure cinnamate of potash. When exposed to cold, cinnameine deposits crystals, which have the same composition as hyduret of cinnamyle, and are therefore an isomeric modification, analogous to benzoine.

According to Richter, balsam of Peru contains two distinct oils, *myroxiline,* insoluble in alcohol, and *myriospermine,* soluble in alcohol. With an alcoholic solution of potash, myriospermine yields an acid resembling cinnamic acid, but different from it, *myriospermic acid.* Balsam of Tolu resembles Balsam of Peru in its constituents. These substances require further investigation.

In the preceding pages we have considered a large number of compound radicals, constituting chiefly the group of radicals analogous in their relations to chlorine : namely, cyanogen; ferrocyanogen and its numerous congeners ; sulphocyanogen ; and mellone. We have only described one radical, *amide,* which has a tendency to produce basic compounds, such as *ammonia, ammonium,* and the *platinised bases ;* and one, *carbonic oxide* or *oxalyle,* the chief tendency of which is to form acid compounds, such as *oxalic, carbonic, rhodizonic, croconic,* and *mellitic* acids. Finally, we have studied three: namely, *benzoyle, salicyle* and *cinnamyle,* whose characteristic is to form essences or fragrant volatile compounds, with hydrogen, acids with oxygen, and peculiar compounds with chlorine, iodine, &c. This last group would appear to have a strong tendency to form acid compounds: for not only is an acid formed by the union of salicyle and oxygen, but the hyduret of salicyle is a decided acid, forming salicylous acid, $C_{14} H_5 O_3$, HO, isomeric with benzoic acid ; instead of hyduret of salicyle, $C_{14} H_5 O_4, H$. Further, the chloride, bromide, and iodide of salicyle, although they contain salicyle, *plus* those elements, are all strong acids, and appear to be in fact *salicylic acid* with 1 eq. of chlorine, &c. substituted for 1 eq. of hydrogen. It is evident that this group of radicals, so well characterised by their hydrogen compounds, does not correspond exactly to any simple radical, but has characters common to different groups of elementary radicals, being, however, analogous in more points to carbon, sulphur, and phosphorus than to any other elements. In studying the decomposition of the compounds of salicyle, we have met with the very remarkable fact of the production from that radical of a series of compounds: namely, anilic acid, nitropicric acid, carbonic acid, &c., probably derivatives of a totally different radical, phenyle; which radical is also met with in numerous other decompositions, and especially in the decomposition of indigo by nitric acid, by alkalies, and by heat, and in the destructive distillation of coal. This is an important consideration, as every day's experience tends to identify with each other the products of decomposition of different and apparently quite unconnected organic compounds, even in cases where these products have been described as different. Another very important fact which has come under our notice is the occurrence of salicylate of oxide of methyle as the chief ingredient in the oil of Gaultheria. Not only is the occurrence of salicylic acid interesting, since this acid was only known before as an artificial product, but the existence, in this oil, of oxide of methyle, hitherto only known as a product of destructive distillation, goes far to confirm the theory which admits this radical, methyle, and others similar to it. All the properties of the oil of Gaultheria entirely agree with the doctrine of its containing two radicals, methyle and salicyle, the former oxidised, as a base; the latter, also oxidised, as an acid.

We now proceed to consider that group of radicals to which methyle belongs, and which are analogous, in their relations, to metals, more than to any other class of elements; forming, like metals, bases with oxygen. This group contains Ethyle, Methyle, Amyle, Glyceryle, Cetyle, and Cacodyle; besides several radicals, derived from the decomposition of these: as, Acetyle from Ethyle, and Formyle from Methyle. These latter, however, belong to that group which are analogous to the combustible metalloids, and form acids with oxygen, instead of bases, like the radicals from which they are derived, and in connection with which they shall be described.

XVI. Ethyle. $C_4 H_5 = Ae$.

Unknown hitherto in a separate form; but very well known as anhydrous oxide, or ether, and hydrated oxide, or alcohol. These compounds have not yet been found as natural products of vegetable life, although it is probable that the fragrance of certain fruits, such as pine-apples, melons, apples, is derived from compounds of ethyle. The compounds of ethyle, especially alcohol, are, however, very abundantly produced by the fermentation of saccharine vegetable juices, such as that of the grape. The alcoholic or vinous fermentation of sugar is a metamorphosis, induced in the sugar by contact with yeast or ferment, which is gluten or fibrine in a state of decomposition. In this metamorphosis, the particles of the ferment only act in communicating mechanical motion to those of the sugar; they do not join the elements of the sugar in producing new compounds, but are decomposed separately; while the elements of the sugar, *plus* a small proportion of the elements of water, form two compounds, alcohol and carbonic acid. $C_{12} H_{11} O_{11} + HO = 2 (C_4 H_5, O + HO) + 4 CO_2$.

1. Oxide of Ethyle. $Ae O = C_4 H_5, O$.

Syn. *Ether. Sulphuric Ether.*—This compound is obtained from alcohol, its hydrate, by heating it gently along with sulphuric or phosphoric acid, which removes the water, or at all events causes the separation of the ether from the water. The best process is as follows: 5 parts of alcohol, of at least 90 per cent., are mixed with 9 of sulphuric acid, and the mixture introduced into a retort, where it is rapidly heated to the boiling-point, and kept at that point, while by means of a bent tube passing through the cork which stops the tubulure of the retort, and furnished with a stop-cock, fresh alcohol is allowed to enter the retort so as to keep the liquid constantly at the original level, flowing in exactly as fast as the ether, &c. distils over. The products are condensed in a powerful refrigeratory, such as Liebig's, figured at p. 285; they consist chiefly of ether, with water in such proportion as would convert the ether into alcohol; and a very little alcohol, sometimes none at all. The operation may be advantageously continued until 31 parts of alcohol, at 90 per cent., have flowed into the retort, and of course an equal volume of ether and water has distilled over.

This process, as to its final result, may be thus expressed. $Ae O, HO + 2 (H O, SO_3) = 2 HO, SO_3 + HO + Ae O$. That is, the action of heat and of oil of vitriol has caused the separation of the ether and the water, which, together, constitute alcohol. And it is to this view of the change, which he considers one of decomposition by contact, that Berzelius applies his theory of a catalytic force. But in reality, the process consists of two stages: the first is the formation of bisulphate of oxide of ethyle (sulphovinic acid) $Ae O, HO, 2 SO_3$; and the second is the decomposition of this by heat into $Ae O$ and $HO, 2 SO_3$. The bisulphate is formed when a mixture of 2 eq. oil of vitriol, 1 eq. alcohol, and from 1 to 3 eq. of water, is heated to about 285°; and at almost precisely the same temperature, the bisulphate is decomposed, especially if the liquid be kept in steady ebullition.

Now, the bisulphate contains anhydrous sulphuric acid, ether, and water, $2SO_3 + AeO + HO$; and when decomposed the sulphuric acid seizes the water, thus preventing the ether from uniting with it to reproduce alcohol. The ether, therefore, distils over; but as, when the bisulphate was formed, ether, AeO, displaced water, HO, from half the oil of vitriol, so now, when the bisulphate is decomposed, and while its water is retained by the 2 eq. of anhydrous acid, the vapours of ether traverse a liquid containing oil of vitriol diluted, both with the water displaced from the other part of it by the ether, and with the water of the alcohol (which at 90 per cent. amounts to 2 eq. for 1 of ether, one combined with the ether to form the alcohol, the other serving to dilute it). Now, a sulphuric acid, thus far diluted, and heated to a temperature even short of 285°, gives off water, and therefore the vapour of ether in passing through this acid, becomes saturated with the vapour of water, without combining with it, and thus ether and water distil over together. At the surface of the boiling, or effervescing liquid, however, the ether produced by the decomposition of the bisulphate is brought into contact with water in the nascent state, also derived from that decomposition, and in this manner, according to Liebig, a little alcohol is reproduced, and distils over with the ether, the ether being produced in the body of the liquid, the alcohol only at the surface. It is certain that a little alcohol generally accompanies the ether, even in the most successful operation; but it is not easy to see how, according to the above explanation, the sulphuric acid which, in the body of the liquid, is able to prevent the ether from combining with water, should fail to do so at the surface. The ether and water, it would appear, are equally in the nascent state in both situations. While, therefore, we admit Liebig's very beautiful explanation of the facts connected with the production of ether, we cannot feel the same certainty in regard to his explanation of the simultaneous occurrence of alcohol. It will now be seen how little necessity there is for resorting to the mysterious agency of catalysis; for the change is not one due to contact alone, but, on the contrary, one depending on strong affinities very nicely balanced, and influenced to a very great extent by the degree of heat employed. The idea that the contact of oil of vitriol caused the ether and water of alcohol to separate, arose from the circumstance that the formation of the bisulphate of ethyle takes place at a temperature quite close to that at which it is decomposed, and that the formation of the bisulphate in this process had been overlooked.

The crude ether is mixed with an alcoholic solution of potash, so as to render it alkaline, and distilled in the vapour-bath, as long as the Sp. G. of the product does not exceed 0·725 at 80°. The ether is then digested for a few days with chloride of calcium, or quicklime, and rectified once more with one of these substances. When pure, oxide of ethyle is a colourless, very mobile, highly refracting liquid, of Sp. G. 0·725° at 60°. It is very volatile, boiling at 76°, and producing intense cold by its evaporation. It has a pungent, cooling, aromatic taste; and a penetrating, agreeable odour. It is very combustible, and its vapour is apt to form dangerous explosive mixtures with air. When oxidised slowly, it yields aldehyde, aldehydic acid, acetic and formic acids.

Ether is used in medicine as a diffusible stimulant, and in chemistry, as a solvent, especially of organic matters: such as fats, fat oils, essential oils, resins, some acids, and some bases.

In its relations to other bodies it exhibits the characters of a base, neutralising acids, and forming compounds which are subject to the laws of double decomposition, like salts of inorganic bases. These salts of oxide of ethyle are, commonly, ethereal liquids; many of them crystallising at low temperatures, and a good many being solid and crystalline at ordinary tempertures. They are often called ethers, with the name of the acid; as, acetic ether, benzoic ether, &c. Those ethers which contain organic acids are for the most part fragrant. The formula for the salts of oxide of ethyle corresponds to that for the salts of potash, &c. Thus, as $\mathrm{KO}, \overline{\mathrm{A}}$ represents acetate, and $\mathrm{KO}, \overline{\mathrm{Bz}}$ benzoate of potash, so $\mathrm{Ae\,O}, \overline{\mathrm{A}}$ or $\mathrm{Ae\,O}, \mathrm{Ac\,O_3}$, and $\mathrm{Ae\,O}, \overline{\mathrm{Bz}}$ or $\mathrm{Ae\,O}, \mathrm{Bz\,O}$ represent the acetate and benzoate of oxide of ethyle.

The analogy between ether and metallic protoxides is further shown in the action of both on hydrochloric acid and its congeners; for while KO, with HCl yields HO and KCl; so $\mathrm{Ae\,O + HCl = HO + Ae\,Cl}$: that is, ether, with hydrochloric acid, yields water and chloride of ethyle. The same is true of the bromide, iodide, &c., and by proper means both the cyanide of ethyle, $\mathrm{Ae\,Cy}$, and the sulphuret of ethyle, $\mathrm{Ae\,S}$, may be obtained. In short, we cannot better connect and classify the numerous facts now known in regard to ether, than by adopting the view which considers it as the basic oxide of ethyle, a compound radical, very analagous to a metal.

2. *Hydrate of oxide of ethyle.* $\mathrm{Ae\,O, HO = C_4\,H_5\,O, HO}$. Syn. *Alcohol.* This compound is formed when ether and water meet in the nascent state, as we shall see occurs when some of the acid salts of ethyle are heated, or otherwise decomposed. But, practically, it is produced entirely from sugar by fermentation. The juice of the grape, or any other saccharine juice, or an infusion of malt, when exposed to the air for a short time,

and then to a temperature of from 40° to 85°, soon enters into fermentation, and a large quantity of carbonic acid is given off, while the sugar totally disappears, and alcohol is found in its place. A pure solution of sugar in water does not ferment, but on the addition of yeast it does so. The juice of the grape and the infusion of malt both contain, besides sugar, some body which plays the part of yeast, or ferment. This is, in the grape juice, fibrine, and in the malt, gluten, both of which readily enter into putrefaction when exposed to air and moisture, and being in this state, their particles in motion, this motion is communicated to the particles of sugar, and the existing equilibrium of affinities being thereby disturbed, new compounds are formed, in this case alcohol and carbonic acid. The subject of fermentation will be afterwards fully discussed: in the mean time, it is to be observed that any similar substance, in a state of putrefaction, will induce the fermentation of sugar; as, for example, putrefying flesh, blood, milk, cheese, white of egg, urine, &c. &c., and that none of these ferments contributes to the production of the alcohol, or carbonic acid, but yield ammonia and other products. Crystallised cane sugar, $C_{12} H_{11} O_{11}$, requires the elements of 1 eq. of water to yield 2 eq. alcohol $C_8 H_{12} O_4$ and 4 eq. carbonic acid $4 CO_2 = C_4 O_8$; and grape sugar, $C_{12} H_{14} O_{14}$, produces, besides the alcohol and carbonic acid, 2 eq. of water. Thus we have $C_{12} H_{11} O_{11} + HO = 2 (C_4 H_6 O_2) + 4 CO_2$; and $C_{12} H_{14} O_{14} = 2 (C_4 H_6 O_2) + 4 CO_2 + 2 HO$.

From the fermented liquid, which, in the case of the grape juice, is wine, in that of malt, beer, ale, or wort, the alcohol is separated by distillation, and being more volatile than water, it predominates in the first portions distilled. These constitute, when from wine, brandy; when from a fermented infusion of malt, whiskey; and when from fermented solution of molasses, rum. In these forms it still contains 30, 40, or more per cent. of water, and a little volatile odoriferous oil. It is again rectified, and the first portions distilled are colourless, and go by the name of spirits of wine. After another rectification they are called rectified spirits of wine. They now contain only alcohol, with from 10 to 20 per cent. of water, which is removed by digesting the spirit with quicklime, and distilling: or by rectifying over dried carbonate of potash, or chloride of calcium.

Pure or absolute alcohol is a colourless, mobile fluid of Sp. G. 0·795 at 60°, and boiling at 173°. It has a burning taste, and a pleasant fruity smell. Rectified spirit of wine, that of 90 per cent., is very similar to it, having the Sp. G. 0·825 to 0·836: ordinary spirit of wine, at 70 per cent., has the Sp. G. 0·880.

Pure alcohol has never been frozen. It is very combustible, and produces, in burning, a very intense heat. Hence spirit of wine is much used for lamps for chemical purposes. Alcohol has a strong attraction for water, and on this account acts as an antiseptic, preserving animal and vegetable substances from putrefaction. The strength of alcohol is ascertained by its specific gravity; and all chemical works contain tables of the relation between the density of the spirit and the per centage.

Alcohol is a powerful diffusible stimulant, and has intoxicating properties. It is much used as a solvent, for many, indeed most vegetable acids and bases, for volatile oils, for resins, and for many salts, even inorganic. Most deliquescent salts are soluble in alcohol, as are the caustic alkalies and iodine. Acids act on alcohol, producing the compound ethers. Solutions made with proof spirit (a mixture of equal volumes of rectified spirit of wine and of water, Sp. G. 0·960), are called tinctures.

3. *Chloride of ethyle*, $Ae\,Cl = C_4\,H_5,\,Cl$, is prepared by saturating alcohol with hydrochloric acid gas, and distilling the mixture in the vapour-bath, collecting the product in a well cooled receiver. It is formed as follows: $Ae\,O,\,HO + HCl = Ae\,Cl + 2\,HO$. It is dried by digestion with chloride of calcium. It is a colourless liquid, Sp. G. 0·874, boiling at 52°, of an aromatic odour, slightly alliaceous. When exposed to the combined action of chlorine and the sun's rays, it yields by substitution a whole series of chlorinised ethers, of which series one extremity is ether $(C_4\,H_5)\,O$; and the other, perchloride of carbon $(C_4\,Cl_5)\,Cl = 2\,C_2\,Cl_3$. With an alcoholic solution of protosulphuret of potassium KS, it gives chloride of potassium and sulphuret of ethyle. $Ae\,Cl + KS = Ae\,S + K\,Cl$. With hydrosulphuret of sulphuret of potassium, it yields *mercaptan*, which is alcohol, in which all the oxygen has been replaced by sulphur. $Ae\,Cl + KS,\,HS = K\,Cl + Ae\,S,\,HS$; the latter, mercaptan, being analogous to $Ae\,O,\,HO$.

4. *Bromide of ethyle*, formed by distilling bromine with alcohol and phosphorus. These are first formed, when the materials are mixed, phosphorous and hydromic acids, and the latter when heated with the alcohol, decomposes it, yielding Ae Br, which resembles the chloride.

5. *Iodide of ethyle*, Ae I, formed by a similar process, is analogous to the two preceding compounds.

6. *Sulphuret of ethyle*, AeS, is prepared, as above stated, from the chloride by sulphuret of potassium. It is a colourless liquid, boiling at 167°, of a strong offensive alliaceous smell.

7. *Hydrosulphuret of sulphuret of ethyle* or *mercaptan*, $Ae\,S,\,HS = C_4\,H_6\,S_2$ or $C_4\,H_5,\,S + HS$. This very remarkable com-

pound is formed when a solution of sulphate of lime and ethyle (sulphovinate of lime) of Sp. G. 1·28, is distilled with its own bulk of a solution of potash of the same density, previously saturated with sulphuretted hydrogen, and converted into KS, HS. The volatile product, after digesting it with a little oxide of mercury and chloride of calcium, to remove sulphuretted hydrogen and water, is mercaptan. Its formation is thus explained: $(CaO, SO_3 + AeO, SO_3) + KS, HS = CaO, SO_3 + KO, SO_3 + AeS, HS$. Pure mercaptan is a colourless liquid, very mobile, boiling at 97°, of Sp. G. 0·842. It has a most penetrating and offensive odour of onions, as it were concentrated, which adheres obstinately to the hair or clothes, so that it is most unpleasant to experiment upon. As above mentioned, it is formed from alcohol by substitution of sulphur for oxygen; and as alcohol is the hydrate of oxide of ethyle, Ae O, H O, mercaptan is the hydrosulphuret of the sulphuret of ethyle, Ae S, H S. The sulphuret of ethyle, AeS, corresponds to the oxide, ether, AeO.

Mercaptan acts strongly on some metallic oxides, especially those of the noble metals, such as mercury, gold, platinum, &c. The metal takes the place of the hydrogen of the sulphuretted hydrogen in mercaptan; thus $MO + (AeS, HS) = HO + (AeS, MS)$. The red oxide of mercury is acted on by mercaptan, and converted into a white crystalline compound, called the mercaptide of mercury; oxide of gold forms a gelatinous white mercaptide; and oxide of lead yields lemon yellow crystals of mercaptide of lead, Ae S, Pb S.

Mercaptan may also be viewed as $H + AeS_2$, in which case the above metallic compounds will have the general formula $M + AeS_2$. Here the supposed radical, the *mercaptum* of Zeise, is bisulphuret of ethyle; so that on either view mercaptan is connected with ethyle.

Zeise has described, under the name of thialic oil or ether, another very fetid compound, which seems to be AeS_3, or persulphuret of ethyle.

Seleniuret and cyanide of ethyle are both volatile alliaceous offensive liquids, formed when sulphate of ethyle and potash is distilled with seleniuret or cyanide of potassium. Sulphocyanide of potassium, alcohol and sulphuric acid, when dissolved together, yield a most offensive volatile liquid, supposed to be, or at all events to contain, sulphocyanide of ethyle. It will be observed that all these compounds of sulphur with ethyle and similar bodies are characterised by odours resembling that of garlic, but so intense and penetrating as to be insupportable. This character is observed in all volatile organic compounds of sulphur, whether artificial, as the above, or natural, as oils of garlic, assafetida, horseradish, &c.

7. Salts of Oxide of Ethyle.

Oxide of ethyle forms both neutral and acid salts. The neutral salts are not at ordinary temperatures decomposed by other salts, like inorganic saline compounds. Thus an alcoholic solution of chloride of calcium does not cause any precipitate in an alcohol solution of oxalate of oxide of ethyle or oxalic ether. But they are easily decomposed by contact with hydrated alkalies, the acid uniting with the alkali, while the oxide of ethyle separates as hydrate, that is, as alcohol. Thus oxalic ether $C_2 O_3, Ae O$, with hydrate of potash, $K O, H O$, yields oxalate of potash $K O, C_2 O_3$, and hydrate of oxide of ethyle, $Ae O, H O$.

Oxide of ethyle has a very great tendency to form double salts, in which there are 2 eq. of the acid, 1 eq. of a basic, and 1 eq. oxide of ethyle. In these salts, the acid, as in the neutral salts cannot be detected by the usual tests; and indeed they may be viewed as simple salts, containing a compound acid, of which oxide of ethyle is a constituent united to the inorganic base. Thus the double sulphate of ethyle and potash, $K O, S O_3 + Ae O, S O_3$, may be viewed as sulphovinate of potash, $K O + Ae O, 2 S O_3$; and sulphovinic acid is, on this view, when separated, $H O + Ae O, 2 S O_3$.

The acid salts of ethyle are on one view double salts, as, for example, the double sulphate formed of sulphate of ethyle, $Ae O, S O_3$, with sulphate of water, $H O, S O_3$. On the other view, they are compound or coupled acids, and the above example becomes, as mentioned in the last paragraph, sulphovinic acid, $H O + (Ae O, 2 S O_3)$, the hydrate of a compound of anhydrous sulphuric acid with ether. These acid salts are decomposed, by boiling with water, into alcohol which distils over, and hydrated acids which remain behind. When distilled with the salts of volatile acids, they yield the ethers of those acids: formiate and acetate of ethyle may be thus obtained. When an acid salt of ethyle is heated with acids not volatile, it often happens that the ethers of these acids are obtained: this is the case with the fatty acids and with some others.

8. *Acid sulphate of oxide of ethyle*, $H O, S O_3 + Ae S O_3$, is also called *sulphovinic acid*, $H O + (Ae O, 2 S O_3)$. Sulphuric acid forms no neutral compound with oxide of ethyle. The acid salt is formed when the vapour of ether is conducted into oil of vitriol, or when oil of vitriol is mixed with alcohol and heated to a certain point. To obtain it pure, the double sulphate of ethyle and baryta (sulphovinate of baryta) in solution, is decom-

posed by sulphuric acid, and the filtered liquid is a solution in water of the acid sulphate. It has a very sour taste, and cannot be concentrated by evaporation, whether at the ordinary temperature or with the aid of heat, without being decomposed into alcohol and sulphuric acid. It forms, with most bases, crystallisable double salts, which are all soluble, so that, for example, the addition of baryta causes no precipitate if the acid be pure. As the acid sulphate itself is called sulphovinic acid, so these double salts are called sulphovinates. It is because all these salts are soluble, that the usual tests cannot detect the sulphuric acid they contain. When, however, their solutions are boiled with a little hydrochloric acid, alcohol is given off, and then the sulphuric acid may be detected as usual. All these salts are decomposed by heat, yielding, according to the temperature, double sulphate of ethyle and etherole, alcohol, sulphurous acid, olefiant gas, and a sulphate as residue, mixed with charcoal. When heated with hydrated alkalies, they yield sulphates and alcohol. The *double sulphate of ethyle and potash* crystallises in shining scales, which are the anhydrous salt, $KO, SO_3 + AeO, SO_3$. The *baryta salt* contains 2 eq. of water of crystallisation, and forms beautiful tabular crystals, as do also the *salt of lime*, and the *salt of lead*, both of which likewise contain 2 eq. of water. These three salts are all composed according to the formula, $MO, SO_3 + AeO, SO_3 + 2$ eq.

9. *Acid phosphate of oxide of ethyle*, or phosphovinic acid, $P_2O_5 \left\{ \begin{matrix} AeO \\ 2HO, \end{matrix} \right.$ is formed in the same way as sulphovinic acid, and obtained pure from the double salt of baryta, $P_2O_5 \left\{ \begin{matrix} AeO \\ 2BaO \end{matrix} \right. + 12HO$. It is a tolerably permanent acid, decomposed only by a high temperature. With bases it forms double salts, in which the 2 eq. water of the acid are replaced by 2 eq. of a protoxide. The *baryta salt*, the formula of which is given above, crystallises in pearly scales.

OXIDE OF ETHYLE WITH NITRIC ACID.

10. Nitrate of Oxide of Ethyle. AeO, NO_5.

When 2 fluid ounces of alcohol, and 1 fluid ounce of pure nitric acid, of Sp. G. 1·4 are distilled together, with the addition of 10 or 20 grains of urea, to destroy any nitrous or hyponitrous acid, the distillation proceeds calmly and smoothly, and the distilled liquor contains water, alcohol, and nitrate of ethyle, which partly separates, towards the end of the process, as a heavy oily stratum, and is more completely separated by the addition of water. It is a colourless liquid, of Sp. G. 1·112; which boils at 185°, and is inflammable, burning with a bright white flame. It is quite insoluble in water, but very soluble in alcohol ; and it possesses a pleasant smell and a sweet taste. An alcoholic solution of potash converts it into alcohol and pure nitrate of potash.

11. Hyponitrite of Oxide of Ethyle. $Ae\,O, N\,O_3$.

Syn. *Nitrous ether.—Nitric ether.* This is best prepared in a state of purity when a current of hyponitrous acid vapours, derived from starch and nitric acid, is passed through weak alcohol, the product being condensed in Liebig's refrigeratory. The ether is washed with water, and dried by means of chloride of calcium. The whole apparatus must be kept cold, otherwise the action is too violent, and the results very complex. When nitrous ether is made by the usual processes, in which ordinary nitric acid is mixed with alcohol, the product always contains a large proportion of aldehyde, and in fact very little of the true ether. The action in this case is as follows, $2\,(C_4\,H_6\,O_2) + N\,O_5 = C_4\,H_3\,O, H\,O$ (aldehyde), $+ 3\,HO + (C_4\,H_5, O + NO_3)$. The pure hyponitrous ether, prepared by Liebig's process, given above, is a pale yellow liquid, boiling at 62°, of Sp. G. 0.947. It has a very agreeable odour of rennet-apples. With an alcoholic solution of potash, it yields alcohol, and pure hyponitrite of potash. The *sweet spirit of nitre* or *spiritus ætheris nitrosi* of the pharmacopœia, is a solution of the impure hyponitrous ether in alcohol.

12. Carbonate of Oxide of Ethyle. $Ae\,O, C\,O_2$.

Syn. *Carbonic ether.* When oxalic ether is acted on by potassium, there are formed several products, one of which is this ether. When pure, it is an aromatic liquid, of Sp. G. 0.975, boiling at 260°. An alcoholic solution of potash converts it into alcohol and carbonate of potash. Chlorine acts on it, forming products to be described when we treat of the action of chlorine on ethers generally.

13. *Double carbonate of ethyle and potash,* $K\,O, C\,O_2 + Ae\,O, C\,O_2$, is formed when dry carbonic acid gas is passed through an alcoholic solution of fused potash. A saline mass is obtained, from which, after washing with ether, alcohol dissolves the double salt, leaving carbonate and bicarbonate of potash. The double salt pours pearly scales, which are decomposed by water into alcohol and bicarbonate of potash.

14. *Oxalate of oxide of ethyle.* $Ae\,O, C_2\,O_3$.—Syn. Oxalic Ether.—This ether is formed by distilling 4 parts of superoxalate of potash, 5 of oil of vitriol and 4 of alcohol at 90 p. c., mixing the product with 4 times its bulk of water, and washing

with water the ether which separates, until all free acid is removed. The ether is then rectified. It is a colourless liquid, of Sp. G. 1·093, boiling at 364°. It has an aromatic smell. If pure, it may be kept under water: but if a trace of alcohol or of oxalic acid be present, it is soon resolved into oxalic acid and alcohol when in contact with water. Fixed alkalies cause the same change. When an excess of ammonia is added to it, oxamide is formed: where the ether is in excess, there is formed a substance in beautiful pearly tables, formerly called oxamethane, but now proved to be oxamate of ethyle. These two reactions are easily explained. In the first case, $AeO, C_2 O_3 + NH_3 = (AeO, HO) + (C_2 O_2, NH_2)$. In the second, half the ether undergoes the above change, and the other half combines with the oxamide formed. $AeO, C_2O_3 + C_2O_2, NH_2 = AeO, C_4 NH_2 O_5$. Chlorine acts on oxalic ether, giving rise to products which will be hereafter described along with the results of the action of chlorine on other ethers.

When to an alcoholic solution of oxalic ether there is added enough of an alcoholic solution of potash or soda to decompose the half of the ether, double salts are obtained, of the formula $MO, C_2 O_3 + AeO, C_2 O_3$. When the alcoholic solution of the double oxalate of ethyle and potash is treated by fluosilicic acid, there is obtained the *acid oxalate of ethyle*, $HO, C_2 O_3 + AeO, C_2 O_3$, which is often called *oxalovinic acid*. The salt of potash, $KO, C_2 O_3 + (AeO, C_2 O_3)$ (*oxalovinate of potash*) forms crystalline scales; soluble in alcohol. The *oxalovinate of baryta* is extremely soluble, and may be used to furnish the other oxalovinates, by acting with it on the soluble sulphates of different bases.

15. *Oxamate of oxide of ethyle*, $C_8 NH_7 O = AeO, C_4 NH_2 O_5 = AeO, C_2 O_3 + Ad, C_2 O_2$, is formed, as above stated, when ammonia is cautiously added to an alcoholic solution of oxalic ether, until a white powder (oxamide) begins to appear. The liquid now yields fine pearly tabular crystals, formerly called oxamethane. It now appears to be oxamate of ethyle, but may also be viewed as oxalate of ethyle, *plus* oxamide. By an excess of ammonia, it is converted into alcohol and oxamide. The action of ammonia on oxalic ether has been explained above.

16. *Sulphocarbonate of ethyle and water*. $AeO, HO, 2CS_2$.—When bisulphuret of carbon is added to a strong alcoholic solution of potash a salt is obtained, in colourless or yellow needles, which is a double sulphocarbonate of ethyle and potash, $KO, CS_2 + AeO, CS_2$. When this salt is acted on by diluted sulphuric or hydrochloric acid, there is obtained a heavy oily liquid.

This is the acid compound in question, $HO, CS_2 + AeO, CS_2$, formerly called xanthic acid, from the yellow colour of its salts. With bases it gives rise to double salts, like that of potash just mentioned; which were called xanthales. The salt of protoxide (suboxide) of copper is lemon yellow.

17. *Bicyanurate of oxide of ethyle,* $(Cy_3 O_3, 3 AeO + Cy_3 O_3, 3 HO) + 3$ aq.: is formed when the vapours of hydrated cyanic acid are brought in contact with a mixture of ether and alcohol. It appears in the form of prismatic brilliant crystals, easily purified from cyamelide by boiling alcohol or even water, which dissolve it and deposit it on cooling.

18. *Benzoate of oxide of ethyle,* or *benzoic ether,* $AeO, Bz'O$, is best formed by distilling 4 parts of alcohol, 2 of benzoic acid, and 1 of strong hydrochloric acid. The ether distils over with alcohol, from which water separates it. When pure, it is an oily, colourless liquid, of a faint agreeable aromatic odour, and an acrid, spicy taste. Its Sp. G. is 1·054, and it boils at about 410°. Chlorine decomposes it, giving rise to several products, probably by substitution.

19. *Hippurate of oxide of ethyle,* or *hippuric ether,* $C_4 H_5, O + C_{18} N H_8 O_5$, is formed by passing a current of hydrochloric acid gas through a solution of hippuric acid in alcohol, and heating the mixture for some time near to its boiling point. The addition of water separates a thick, heavy oil, which when purified from alcohol and hydrochloric acid, and placed in vacuo, along with sulphuric acid, forms a solid crystalline mass, composed of silky needles. It is decomposed, like other ethers, by alkalies, and by boiling with water.

20. *Salicylate of oxide of ethyle,* $C_4 H_5, O + C_{14} H_5 O_5$, is obtained by distilling 2 parts of alcohol, 1½ of salicylic acid, and 1 of sulphuric acid. When purified from alcohol, acid, and water, it is a colourless oily fluid, having a sweet smell like that of the corresponding compound of methyle, which occurs naturally in the oil of *Gaultheria procumbens.* It is heavier than water, and boils at 437°. Like the oil of Gaultheria, it plays the part of an acid, forming with bases crystallised soluble salts. When exposed to a high temperature with caustic baryta, it yields carbonic acid, and an oil analogous to that obtained from the methyle compound, probably $C_{18} H_{10} O_2$. When fuming nitric acid is added drop by drop to the salicylic ether; it dissolves it with a deep red colour: water now separates an oil, which soon concretes into a solid mass, which when dissolved in hot alcohol, yields on cooling, yellow silky needles. These are *indigotate or anilate of oxide of ethyle,* $C_4 H_5, O + C_{14} N H_4 O_9$. By the further action of nitric acid, carbazotic or nitropicric acid

is obtained. The indigotic ether dissolves in potash and soda, apparently like the salicylic ether, playing the part of an acid. Indigotic ether does not dissolve in ammonia: left in contact within close vessels, it finally disappears: alcohol is reproduced, and there is formed a new product, *anilamide*, $C_{14} N_2 H_6 O_8$, which, when pure, forms brilliant yellow crystals. When boiled with potash, anilamide yields anilate (indigotate) of potash, and gives off ammonia; for, $C_{14} N_2 H_6 O_8 + 2 HO = NH_3 + C_{14} H_4 NO_9, HO$. Bromine acts on salicylic ether, producing two compounds: monobromuretted salicylic ether, $C_{18} H_9 Br O_6 = C_4 \left\{\begin{matrix} H_4 \\ Br \end{matrix}\right. O + C_{14} H_5 O_5$: and bibromuretted salicylic ether, $C_{18} H_8 Br_2 O_6 = C_4 \left\{\begin{matrix} H_3 \\ Br_2 \end{matrix}\right. O + C_{14} H_5 O_5$. The former crystallises in fine needles: the latter in large pearly scales, which, when melted, form on cooling a most beautiful crystallisation, formed of large and perfect cubes, like those of bismuth.

COMPOUNDS OF ETHYLE OF UNCERTAIN CONSTITUTION.

1. *Chloro-carbonic Ether*, $C_6 H_5 Cl O_4 = C_4 H_5, O + C_2 \left\{\begin{matrix} O_3 \\ Cl \end{matrix}\right.$? Formed when absolute alcohol is placed in contact with chlorocarbonic acid gas. It appears as an oily liquid, of Sp. G. 1·133, boiling at 200°. It is formed as follows: 2 eq. of chlorocarbonic acid and 1 of alcohol, losing 1 eq. hydrochloric acid, yield 1 eq. of the new ether. $C_2 O_2 Cl_2 + C_4 H_6 O_2 = H Cl + C_6 H_5 Cl O_4$. It may be viewed as a compound of oxide of ethyle, with a peculiar acid $C_2 \left\{\begin{matrix} O_3 \\ Cl \end{matrix}\right.$; or as carbonic ether $C_5 H_5 O_3$, *plus* 1 eq. chlorocarbonic acid, $C \left\{\begin{matrix} O \\ Cl \end{matrix}\right.$.

2. *Urethane*, $C_6 H_7 NO_4$, is formed by the action of ammonia on the preceding compound, along with sal ammoniac, from which it is separated by being sublimed, or rather distilled, when it passes over at a gentle heat, as a liquid which crystallises on cooling. It is very soluble in water and alcohol, and yields very large crystals. It may be viewed as chlorocarbonic ether, in which amide, NH_2 has been substituted for the chlorine: $C_4 H_5, O + C_2 \left\{\begin{matrix} O_3 \\ NH_2 \end{matrix}\right.$. It is formed as follows: $C_6 H_5 Cl O_4 + 2 NH_3 = (NH_3, H Cl) + C_6 H_7 NO_4$. It may also be viewed as formed of 2 eq. carbonic ether and 1 eq. urea: for $2 (C_5 H_5 O_3) + (C_2 N_2 H_4 O_2) = 2 (C_6 H_7 NO_4)$. Finally, it has the composition of dry lactate of ammonia, $NH_3 + C_6 H_4 O_4$, or rather a compound of ammonia with sublimed lactic acid.

METAMORPHOSES OF THE COMPOUNDS OF ETHYLE.

When ether or alcohol is passed in vapour through a red hot tube, it yields aldehyde, water, olefiant gas, and marsh gas, $3\,(C_4\,H_5\,O) = C_4\,H_4\,O_2 + HO + 3\,C_2\,H_2 + C_2\,H_4$: or $2\,(C_4\,H_5\,O) = C_4\,H_4\,O_2 + C_2\,H_2 + C_2\,H_4$. By the action of chloride of zinc on alcohol, there are formed water, and two liquid carbo-hydrogens, $C_8\,H_7$ and $C_8\,H_9$, together $C_{16}\,H_{16}$, that is, olefiant gas, or an isomeric modification of it. Now ether and alcohol both contain the elements of water and of olefiant gas; for alcohol is $C_4\,H_6\,O_2 = 2\,HO + C_4\,H_4$; and ether is $C_4\,H_5\,O = HO + C_4\,H_4$.

In the manufacture of ether there occur two liquids, one of which is called *oil of wine*, which is $C_{16}\,H_{15}$, or very nearly the proportions of olefiant gas, according to the only analysis we have. The other is called the sweet or heavy oil of wine, and is a compound of sulphuric acid with ether, and a body having the same composition in 100 parts as olefiant gas. Sweet oil of wine is $2\,SO_3 + AeO + C_4\,H_4$; and as this body, $C_4\,H_4$, is called etherole, the compound is named the double sulphate of oxide of ethyle and of etherole. This latter is produced, along with sulphovinic acid, from the reaction of 4 eq. dry sulphuric acid and 3 eq. ether. $4\,SO_3 + 3\,AeO = (2\,SO_3,\ AeO,\ HO) + (2\,SO_3,\ AeO,\ C_4\,H_4)$. The same compound is formed when sulphovinate of lime is heated, but is accompanied by alcohol, sulphurous acid, olefiant gas, and a residue of sulphate of lime and charcoal. $2\,(CaO,\ AeO,\ 2\,SO_3) = (2\,SO_3,\ AeO,\ C_4\,H_4) + HO + 2\,(CaO,\ SO_3)$; and again, $2\,(CaO,\ AeO,\ 2\,SO_3) = 2\,(CaO,\ SO_3) + 2\,SO_2 + C_4\,H_6\,O_2 + C_2\,H_2 + C_2 + 2\,HO$.

The sweet oil of wine is an oily liquid, quite neutral. It boils at 536°, and has the Sp. G. 1·133. When heated with water it gives off etherole as an insoluble oil, while the liquid contains pure sulphovinic acid. When the etherole thus separated is exposed to cold, it deposits crystals of *etherine*, a compound isomeric with etherole and with olefiant gas.

ETHIONIC, ISETHIONIC, METHIONIC AND ALTHIONIC ACIDS.

These acids are formed by the action of sulphuric acid on ether and alcohol under various circumstances. When anhydrous acid, SO_3 acts on alcohol, or when olefiant gas is absorbed by that dry acid, there is formed a compound, $2\,SO_3 + C_4\,H_4$, in crystals, which, when put into cold water, produce ethionic acid, $2\,SO_3,\ C_4\,H_5\,O$. When this solution is heated, 2 eq. of sulphuric acid and 1 of alcohol separate from one half, and there is formed from the other half isethionic acid, $2\,SO_3,\ C_4$

H_5O, or rather $S_2O_5, C_4H_5O_2$. Ethionate of baryta, formed by adding baryta to the acid before boiling, is $2\,SO_3, C_4H_5O, BaO$. From it, all the other ethionates may be made. The salts of isethionic acid, like those of ethionic acid, have the same composition in 100 parts as the sulphovinates; but as they contain hyposulphuric acid, their formula is $S_2O_5, C_4H_5O_2 + MO$. They crystallise with remarkable facility. When, in acting on ether with anhydrous sulphuric acid, the mixture gets too hot, there is formed a new acid, *methionic acid*, the baryta salt of which is $S_2C_2H_3O_7, BaO$, or $S_2O_5, C_2H_3O_2 + BaO$. This acid apparently bears the same relation to oxide of methyle, C_2H_3O, as isethionic does to ether, C_4H_5O. When oil of vitriol in great excess, is heated with alcohol, olefiant gas is given off, and the residue is found to contain an acid, the salts of which have the very same composition as the sulphovinates, but differ in crystalline form. This acid is called *althionic acid*. It is highly probable that the althionates are mixtures or compounds of sulphovinates with isethionates, just as the salts of ethionic acid appear to contain sulphovinates and isethionates or compounds isomeric with these. The two compounds which seem to be distinct and independent are sulphovinic acid, $(AeO, HO, 2\,SO_3)$ and isethionic acid, isomeric with it, but probably arranged as (HO, AeO_2, S_2O_5); the salts of the former being strictly double sulphates of ethyle and bases, $(MO, SO_3 + AeO, SO_3)$; and those of the latter being $MO + (AeO_2, S_2O_5)$. Whatever explanation may be given of the fact, it is a fact, that the ethionic and althionic acids and their salts have the same empirical composition as these two acids and their salts, at least according to the best analyses we have.

PRODUCTS OF THE OXIDATION OF ETHYLE AND ITS DERIVATIVES.

The oxidation of alcohol and of ether may be effected in a great variety of ways, and the products are rather numerous, varying according to the amount of oxygen taken up. Thus we have, first aldehyde, then acetic acid, formic acid, oxalic acid, and finally carbonic acid and water. The first effect of oxidation is to destroy the radical ethyle, giving rise to a new and less complex radical, *acetyle* $= C_4H_3$. Afterwards we obtain compounds of the still less complex radical, *formyle*, $= C_2H_3$, and lastly, compounds of the simple radicals carbon and hydrogen.

We shall here consider, first, the radical acetyle and its compounds: bearing in mind that while derived from the basic radical ethyle, acetyle has no basic characters whatever, but is, on the contrary, a most distinctly acidifiable radical.

XVII. ACETYLE. $C_4\ H_3 = Ac.$

Acetyle is unknown in a separate form, but is easily obtained in the form of hydrated protoxide, or *aldehyde,* and hydrated peroxide, or *acetic acid.*

1. Hydrated Oxide of Acetyle, or Aldehyde. $(C_4 H_3) O, HO. = Ac O, HO.$

Aldehyde is formed when ether or alcohol is passed through a red-hot tube, or when ether or alcohol are oxidised by nitric acid, or by chlorine, &c. In these cases it is not pure; but it may be obtained quite pure by distilling 2 parts of the compound of aldehyde and ammonia dissolved in 2 parts of water, along with a mixture of 3 parts of oil of vitriol and 4 of water, and rectifying at a temperature of about 80°, over chloride of calcium.

It is a clear, colourless liquid, of a peculiar and powerful etherial odour, of Sp. G. 0·79 at 65°, and boiling at 70°. It mixes in all proportions with water, alcohol, and ether, and is neutral and inflammable. In contact with the atmosphere it rapidly absorbs oxygen, passing into hydrated acetic acid: for $C_4 H_3, O + HO$, with O_2, at once produce $C_4 H_3, O_3 + HO$; or $AcO, HO + O_2 = AcO_3, HO$.

When heated with caustic potash it is rapidly converted into the brown matter called resin of aldehyde. If gently heated with oxide of silver and water, part of the oxide is reduced without effervescence, coating the glass tube with a bright surface of silver, while the water is found to contain a salt of silver, the acid of which contains less oxygen than acetic acid: this is aldehydic or lampic acid, $C_4 H_3 O_2, HO$, or AcO_2, HO. The solution of aldehydate of silver, if filtered and heated to boiling, again deposits metallic silver, while the aldehydic acid becomes acetic.

When long kept, even in sealed tubes, aldehyde is transformed into two isomeric modifications, namely, *metaldehyde,* a hard crystalline inodorous solid; and *elaldehyde,* which is liquid.

Aldehydite of ammonia. $C_4 H_3, O + NH_3 + HO$. Aldehyde has no basic characters, and rather exhibits a tendency to the acid character, in combining with ammonia, as it does directly, to form a crystallised compound. To prepare it, as the substance from which aldehyde is obtained, 6 parts of oil of vitriol, 4 of water, 4 of alcohol, and 6 of peroxide of manganese, in fine powder, are distilled together. The crude product is twice rectified over chloride of calcium; it is now aldehyde, containing a little water, alcohol, and acetic and formic ethers; and this liquid, when mixed with ether, and saturated with ammoniacal gas, yields crystals of the new compound, which are washed with ether. These crystals become brown on being kept, even in close vessels, and acquire the smell of burnt feathers. They dissolve in water and alcohol, but hardly in ether. Nitrate of silver forms, in the concentrated solution, a precipitate, insoluble in alcohol, which, when heated, is reduced.

2. Acetal. $C_8 H_9 O_3 = C_4 H_3, O + C_4 H_5, O + HO = AcO + AeO + HO.$

Is formed by the action of the oxygen of the air on the vapours of alcohol, under the influence of the black powder of platinum. It is a colourless very mobile liquid, Sp. G. 0·825, boiling at 203°. It might, according to its composition, be a compound of 3 eq. oxide of ethyle, and 1 eq. acetic acid; for $3 (C_4 H_5, O) + C_4 H_3 O_3 = C_{16} H_{18} O_6 = 2 (C_8 H_9 O_3)$. But the action of potash, which forms resin of aldehyde, and of oil of vitriol, which blackens and thickens it as it does aldehyde, indicate pretty certainly the presence of aldehyde; and we therefore prefer the formula above given, which makes acetal a compound of aldehyde and oxide of ethyle.

The resin of aldehyde, formed by the action of potash on aldehyde, is little known. *Elaldehyde*, an isomeric form of aldehyde, which is liquid at ordinary temperatures, but solid at 32°, has a formula exactly triple that of aldehyde, $C_{12} H_{12} O_6$. *Metaldehyde*, the other isomeric modification, which, like the preceding, spontaneously forms in aldehyde when kept, has no doubt a similar relation in its formula to that of aldehyde; but its precise formula is not yet known. The density of its vapour would settle the point. It forms very hard prisms, which sublime at 248° without melting. It is worthy of notice that aldehyde, like the corresponding chlorine compound, formed by substitution, *chloral*, $C_4 Cl_3 O + HO$, undergoes very easily, and even spontaneously, these very singular metamorphoses. This indicates a relation in the constitution of these bodies, which cannot be overlooked.

3. Acetylous Acid. $(C_4 H_3) O_2, HO = Ac O_2, HO.$

Syn. *Aldehydic Acid. Lampic Acid.* It has already been stated that this acid is obtained in combination with oxide of silver, when aldehyde is gently heated with excess of that oxide in water. The solution, when the silver has been separated by sulphuretted hydrogen, contains the acetylous acid very diluted. It is very easily decomposed, especially by heat, into acetic acid and a brown resin, like that of aldehyde. When the acetylite or aldehydate of silver is decomposed by baryta, so as to precipitate all the oxide of silver, and the acetylite of baryta is now heated with the precipitated oxide of silver, the metal is reduced, and *acetate* of baryta is now found in the solution. This demonstrates the relation of acetylous to acetic acid : for $BaO, AcO_2 + AgO = BaO, AcO_3 + Ag$. This acid is one chief ingredient of the acid produced by the slow combustion of ether in the lamp with a spiral of platinum wire on the wick, the platinum continuing red-hot, but no flame appearing, and which acid is called lampic acid.

Aldehyde is a constant ingredient of the nitrous ether of the pharmacopœias.

4. Acetic Acid. $C_4 H_3, O_3 + HO = AcO_3, HO$.

SYN. *Acetylic acid.—Pyroligneous acid.—Vinegar.*—This important acid is formed in two principal ways : first, by the oxidation of alcohol ; and, secondly, by the destructive distillation of wood. Wine, beer, and other fermented liquors, if exposed to the air, under certain circumstances, undergo what is erroneously termed the acetous fermentation ; that is, they attract oxygen from the air, undergo eremacausis of the alcohol they contain, and, after a time, contain no alcohol, but in its place acetic acid ; they are, in fact, converted into vinegar. The ultimate change is very simple : $C_4 H_6 O_2 + O_4 = C_4 H_3 O_3, 3 HO, = AcO_3, HO + 2$ aq. But we have already seen that there are intermediate steps in the process. The first effect of the oxygen is to remove from the alcohol, or rather from the ethyle in it, 2 eq. of hydrogen, thus leaving the radical acetyle, $C_4 H_3$, in the place of the ethyle $(C_4 H_5) O, HO + O_2 = (C_4 H_3) O, HO +$ 2 aq. In this stage, alcohol is simply converted into aldehyde, while 2 eq. of water are formed. In the next stage, the hydrated protoxide of acetyle (the aldehyde), or rather the radical $C_4 H_3$, takes up 2 additional equivalents of water, and thereby becomes acetic or acetylic acid $(C_4 H_3) O, HO + O_2 = (C_4 H_3) O_3, HO$.

Such being the action of the oxygen of the air on alcohol, it is obvious that the process of acetification is no fermentation, but a case of eremacausis or slow combustion. But, as was formerly explained, the state of eremacausis is induced by contact of a body in that state or even in the state of fermentation or putrefaction, and the presence of a ferment is required to commence the process of eremacausis of alcohol. Pure alcohol, exposed to air alone, is not acetified : but if its vapour, mixed with air, come in contact with platinum powder, eremacausis is induced. Hence, if alcohol be placed in a flat basin under a bell jar, beside a small flat dish containing platinum black, the bell jar is, in a few seconds, filled with the pungent smell of aldehyde ; and in an hour or two, the acetification is nearly complete. Here the platinum, by virtue of its singular power of causing gases or vapours to unite on its surface, acts as a ferment, or, as it may be called, an excitant, inducing the slow combustion, and acting as a carrier of oxygen from the air to the alcohol.

In wine or beer, there is present an actual ferment in the shape of gluten or fibrin, at least in all cases where the vinous fermentation has not decomposed the whole of the ferment. In these cases, exposure to the air for a short time causes the decomposition of the gluten, &c., to recommence; and this state of decomposition, being mechanically communicated in the shape of motion to the particles of alcohol, slow combustion commences, and continues till every trace of alcohol has been acetified, when the process is arrested for want of fuel, that is, of alcohol. Where, in the fermentation of wine (as sherry), or of beer (as Bavarian beer), all ferment has been destroyed or removed, these liquors do not become sour when exposed to air: and if we wish to acetify them, we must add yeast or some other ferment. So, also, when we wish to make strong vinegar by the acetification of brandy or of whiskey, we have to add a ferment, such as yeast, and expose the mixture to a certain temperature in open vats. By carefully attending to all these principles, the process of acetification may be very much abridged. The following is the rapid process now followed on the Continent. There is made a mixture of 1 part of alcohol at 80 p. c., 4 to 6 parts of water, and $\frac{1}{1000}$ of a ferment such as vinegar, honey, or must of beer. A large, high barrel is packed with twigs or shavings of beech, previously soaked in strong vinegar; and holes are drilled in the middle and upper part of the barrel to admit a free circulation of air. The mixture is now warmed to from 75° to 80°, and made to trickle slowly upon the shavings and through the barrel, thus exposing an immense surface to the air. The temperature rises rapidly to 95° or 105°, and if a proper supply of air be given, continues at that point during the operation. When the mixture has been three or four times passed through the barrel, it is found perfectly acetified: this may take place in from 24 to 36 hours. Should the supply of fresh air, that is, of oxygen, be deficient, much aldehyde is produced, which, from its volatility, is carried off as vapour and lost. This was long a source of great loss to the makers, and the cause could not be traced, until Liebig, by the discovery of aldehyde, explained it, and showed how to avoid the loss, by giving a due supply of air. The manufacturer now obtains, as nearly as can be expected, the theoretical quantity of vinegar from his spirits. Any aromatic substance, or essential oil, or even a trace of wood vinegar (contaminated with kreosote, &c.) will arrest the progress of acetification.

The peculiar pleasant smell of good vinegar, in addition to that of pure diluted acetic acid, is owing to the presence of acetic ether. Distilled vinegar is a tolerably pure but weak acetic acid; but to obtain acetic acid pure and strong, we must have recourse to the salts of acetic acid, which, when distilled with moderately strong sulphuric acid, yield pure acetic acid, mixed with more or less water.

The pyroligneous acid is contaminated with pyroxylic spirit and with oil of tar. When combined with soda, lime, or oxide of lead, these salts may be easily purified by crystallisation, and by heating them so far as to expel or destroy the oily impurities. The pure salts, distilled with sulphuric acid, yield acetic acid, identical with that from true vinegar.

Hydrated acetic acid, radical vinegar, or crystallisable acetic acid, AcO_3, HO, is obtained by distilling 3 parts of dry powdered acetate of soda with 9·7 of oil of vitriol, as pure and concentrated as possible: $\frac{1}{8}$ of the acid distils over by the heat spontaneously developed in the mixture; a gentle heat expels the rest. The product is rectified and exposed to a cold of 23° or 24°, when crystals of the hydrate are formed in a weaker liquid. The crystals are allowed to drain, and then melted, and again exposed to cold. The crystals of this second operation are generally free from all superfluous water. At temperatures below 60°, hydrated acetic acid is solid, at 62° or 63° it melts, forming a liquid which sometimes continues liquid at a much lower temperature, and then crystallises from some very trifling cause. The Sp. G, of the liquid is 1·063; it boils at 248°; has a pungent, peculiar, but agreeable smell, and a burning acid taste. It raises a blister on the skin, and soon produces a painful sore, like a mineral acid. It is miscible in all proportions with water, alcohol, and ether. It dissolves camphor and essential oils; and the aromatic vinegar is a solution of camphor with a little oil of lemons and bergamot, &c. Strong acetic acid, in this form, is used as a diffusible stimulant, applied to the nostril in faintness or sickness. It may be used, also, externally as a very powerful rubefacient and epispastic. The hydrated acid is combustible. It is decomposed by anhydrous sulphuric acid, yielding a new acid, *sulphacetic acid:* also by chlorine, yielding by substitution *chloracetic acid.* The vapour of acetic acid, passed through a red-hot tube, yields carbonic acid and acetone, $C_3 H_3 O$: the same transformation occurs when acetic acid is heated with bases.

The salts of acetic acid are, almost without exception, soluble in water: the acetates of silver and protoxide of mercury are sparingly soluble. The formula for the neutral acetates is $MO, C_4 H_3 O_3$ or $M, C_4 H_3 O_4$. There are hardly any acid salts; but a considerable number of basic salts, as basic acetates of lead and copper.

Acetate of oxide of ethyle or *acetic ether*, AeO, AcO_3, is easily prepared by distilling 10 parts of acetate of soda, 16 of oil of vitrol, and 6 of alcohol. The product is rectified over lime and chloride of calcium. It may also be obtained by distilling any sulphovinate with strong acetic acid. In either case, acetic acid is brought in contact with nascent ether, and combines with it. Acetic ether is a colourless liquid of a refreshing odour, very combustible. It boils at 165°; its Sp. G. is 0·89. It is easily decomposed by alkalies, yielding an acetate and alcohol. Acids also decompose it. It is always present, in small quantity, in wine vinegar, which owes its flavour to this compound.

Acetate of ammonia. There is a well-known febrifuge and diaphoretic remedy called the *spirit of Mindererus*, which is a diluted solution of acetate of ammonia, formed by neutralising distilled wine vinegar with carbonate of ammonia. A more uniform preparation, although stronger than that usually employed here, is made by neutralising 6 parts of aqua ammoniæ, Sp. G. 0·96, with strong acetic acid, and adding enough water to make up 24 parts. This, being uniform, can easily be reduced if desirable. There is an acid acetate of ammonia, which forms deliquescent needles. *Acetate of potash*, KO, AcO_3, is obtained as a fibrous crystalline mass, very deliquescent, which has a warm saline taste. It is much used as a diuretic. When heated with arsenious acid, it yields oxide of cacodyle; a substance of most remarkable composition and characters, $C_4H_6As_2,O$. *Acetate of Soda* NaO, AcO_3+6 aq. is formed from pyroligneous acid, and is the form in which the acid is brought in order to be purified from oil of tar. The salt is melted at a moderate heat, and roasted, then redissolved, filtered through charcoal, evaporated, again melted, and so on, until it becomes snow-white. 10 parts of the crystals of the salt after the first fusion, while still slightly coloured, being distilled with 6 of oil of vitriol, yield what is called wood vinegar, sufficiently pure for use, but requiring 7 waters to reduce it to the average strength of wine vinegar. Acetates of baryta, strontia and lime all crystallise readily. The first is used as a test; the last in the manufacture of acetic acid and all other acetates from pyroligneous acid. *Acetate of alumina*, $Al_2O_3, 3AcO_3$, prepared by mixing solutions of alum and acetate of lead (or of baryta) is very soluble. It is much used in the above form, containing sulphate of potash, as a most valuable mordant in dyeing and calico printing. When heated it deposits an insoluble basic salt, which adheres tenaciously to the cloth, and afterwards combines firmly with the colouring matter. The pure acetate of alumina, formed from sulphate of alumina and acetate of baryta, is not so decomposed by heat, but requires the presence of a neutral salt. *Acetate of manganese*, MnO, AcO_3, formed by acting on sulphate of manganese by acetate of lime, is much used in calico printing, as it gives with bleaching liquor a rich bronze brown. *Aceteat of zinc*, $ZnO, AcO_3, + 3$ aq. is used in medicine and pharmacy. *Acetate of protoxide of iron*, FeO, AcO_3 is used as a mordant. *Acetate of peroxide of iron*, $Fe_2O_3, 3 AcO_3$, is formed by precipitating acetate of lead with persulphate of iron. It has the same valuable properties as acetate of alumina, depositing a basic salt, when heated with neutral salts, and is much prized as a mordant. *Acetate of lead;* a. *neutral*, Syn. *Sugar of lead;* is best prepared by dissolving litharge in acetic acid, and crystallising. It has a sweet astringent taste, and is much used as an astringent and styptic in diarrhœa, dysentery, and various hæmorrhages. It is poisonous, especially where it forms carbonate: it ought therefore never to be given without abundance of vinegar being taken by the patient. The crystals are $PbO, AcO_3 + 3$ aq. b. *sesquibasic*, $3 PbO + 2 AcO_3$ soluble pearly scales. c. *tribasic* or *subacetate of lead* is formed in crystals by mixing 1 vol. of aqua ammoniæ with 5 of a cold saturated solution of the neutral salt, and setting it aside. It forms long needles. The solution, or Goulard's extract, is made by digesting 7 parts of litharge with 6 of sugar of lead and 30 of water, till the oxide, which is not dissolved, has become white. It is much used as a lotion, and to precipitate gum, organic acids, albumen, caseine, extractive matter, &c., from organic mixtures and solutions. Its formula is $3 PbO + AcO_3$. d. *sexbasic*, formed by adding the last or any of the previous acetates of lead to an excess of ammonia. It forms a crystalline powder very sparingly soluble, which is $6 PbO + AcO_3$. It usually exists in white lead, along with carbonate of lead.

Acetate of Copper. a. *neutral;* appears in two forms: as dark green oblique rhombic prisms, becoming opaque in air: $CuO, AcO_3 +$aq.: and as dark blue transparent crystals of great beauty, $CuO, AcO_3 + 5$ aq. These latter, heated to 86°, lose 4 eq. of water, and fall to a powder of the green salt. b. *bibasic* or *verdigris*, $2 CuO + AcO_3 + 6$ aq.$= CuO, AcO_3, 5$ aq.$+ CuO, HO$. Verdigris is prepared by a tedious process, and is seldom pure, containing usually different basic acetates. c. *sesquibasic*, $3 CuO, 2 AcO_3 + 6$ aq. d. *tribasic*, $6 CuO, 2 AcO_3 + 3$ aq. The two last occur in the verdigris of commerce. All these salts are poisonous.

Schweinfurt or Vienna green is a double salt, formed of acetate and arsenite of copper; $CuO, AcO_3 + 3 (As_2O_3, CuO)$ is formed when 10 parts of verdigris, suspended in water, are left to digest for 24 hours, after mixing them with a hot solution of 8 parts of arsenious acid in 100 of water. A dirty green precipitate first appears, which on standing changes to a most beautiful green, much used as a paint.

Acetate of protoxide of mercury is obtained in sparingly soluble silvery scales by adding acetate of potash to protonitrate of mercury, both hot. It blackens when exposed to light. It is used in medicine, especially on the Continent.

Acetate of silver, AgO, AcO_3, very much resembles the preceding salt. It is occasionally used as a test. It is very sparingly soluble.

ACTION OF CHLORINE, BROMINE, ETC., ON ETHYLE, ACETYLE, AND THEIR DERIVATIVES.

1. Oxide of Ethyle and Chlorine.

When dry chlorine is made to act on ether, with the aid of the sun's rays, there are produced several compounds. The first is a heavy oily liquid, oxychloride of acetyle, $C_4 H_3 \left\{ \begin{matrix} O \\ Cl_2 \end{matrix} \right.$; which is dry acetic acid with 2 eq. of oxygen replaced by 2 eq. of chlorine. With water, it forms acetic and hydrochloric acids. When the action is pursued, there is obtained a compound $C_4 Cl_5 O$, which is ether, in which all the hydrogen is replaced by chlorine. The first compound may be connected with this one by being viewed as ether in which hydrogen is partially replaced by chlorine, $C_4 \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right. O$. Finally there is obtained a crystallisable solid compound, $C_4 Cl_6$, which may be represented as $C_4 Cl_5, Cl$, showing that the oxygen of ether is also here replaced by chlorine. This last body is chloride of carbon, $C_2 Cl_3$ for $C_4 Cl_6 = 2\ C_2 Cl_3$. Besides these compounds there are others formed at the same time, more difficult to separate, and which are doubtless the intermediate links of the chain of substitutions, beginning with ether $C_4 H_5, O$, and ending with *chloride of carbon*, $C_4 Cl_5, Cl$. The other members of the series which are more easily obtained by the action of chlorine on *chloride of ethyle*, (see below, p. 376), are, $C_4 H_5, Cl$, chloride of ethyle: $C_4 \left\{ \begin{matrix} H_4 \\ Cl, \end{matrix} \right. Cl$: $C_4 \left\{ \begin{matrix} H_3 \\ Cl_2, \end{matrix} \right. Cl$: $C_4 \left\{ \begin{matrix} H_2 \\ Cl_3, \end{matrix} \right. Cl$: $C_4 \left\{ \begin{matrix} H \\ Cl_4, \end{matrix} \right. Cl$; and as the compound $C_4 Cl_5 O$ is formed, it is probable that there is another series, beginning with ether, and ending with $C_4 Cl_5, O$, in which the oxygen remains unchanged. The above are not all cases of substitution with preservation of the type; for the compound $C_4 \left\{ \begin{matrix} H_3 \\ Cl_2, \end{matrix} \right. O$, may very likely be $C_4 H_3 \left\{ \begin{matrix} O \\ Cl_2 \end{matrix} \right.$ belonging to the type of acetic acid, rather than that of ether. These compounds are as yet but little known: it is obvious that the simultaneous occurrence of so many similar compounds must render the study of them exceedingly complicated and difficult.

The body $C_4 H_3 \begin{cases} O \\ Cl_2 \end{cases}$, or oxychloride of acetyle, when acted on by sulphuretted hydrogen, yields two new compounds, in which its chlorine is partially or entirely replaced by sulphur. Both are crystalline: one, the oxysulphuret of acetyle, $C_4 H_3 \begin{cases} O \\ S_2 \end{cases}$ forms large colourless prisms: the other, oxychlorosulphuret of acetyle, $C_4 H_3 \begin{cases} O \\ Cl^5 \end{cases}$, forms yellow tabular crystals.

2. Salts of oxide of ethyle with chlorine.

When chlorine acts on these salts or ethers, their oxide of ethyle is acted on as if separate, but in many cases the acids remain combined with the new chlorinised compounds: or the acids also are acted on, and the products derived from them combine with those derived from the ether.

Acetic ether yields a compound $C_8 H_6 Cl_2 O_4$, which may be viewed as $C_4 H_3 \begin{cases} O \\ Cl_2 \end{cases} + C_4 H_3 O_3$, that is, acetate of the oxychloride of acetyle. When the compound is further exposed to the action of chlorine at a high temperature, it yields a series of compounds, in which its hydrogen is gradually replaced by chlorine, till the compound $C_8 Cl_8 O_4$ is left, which is called perchloruretted acetic ether. Acetic ether is $C_8 H_8 O_4$; and we have the acetate of oxychloride of acetyle $C_8 \begin{cases} H_6 \\ Cl_2 \end{cases} O_4$; then $C_8 \begin{cases} H_5 \\ Cl_3 \end{cases} O_4$: $C_8 \begin{cases} H_4 \\ Cl_4 \end{cases} O_4$: $C_8 \begin{cases} H_3 \\ Cl_5 \end{cases} O_4$: $C_8 \begin{cases} H_2 \\ Cl_6 \end{cases} O_4$: $C_8 \begin{cases} H \\ Cl_7 \end{cases} O_4$: and $C_8 Cl_8 O_4$. The two last can be obtained with certainty pure: the others, after $C_8 \begin{cases} H_6 \\ Cl_2 \end{cases} O_4$, are so mixed that it is very difficult to obtain them pure enough for analysis.

When *benzoic ether*, AeO, BzO, is acted on by chlorine, it loses 2 eq. hydrogen, and 1 eq. oxygen, and takes up 3 eq. chlorine, producing a compound which may be viewed as containing chloride of benzoyle and oxychloride of acetyle, $BzCl + C_4 H_3 \begin{cases} O \\ Cl_2 \end{cases} = C_{18} H_8 Cl_3 O_3$.

Oxalic ether, exposed to the action of chlorine under the influence of the direct rays of the sun, loses all its hydrogen, which is replaced by chlorine. $(C_4 H_5) O, C_2 O_3$ thus becomes $(C_4 Cl_5) O, C_2 O_3$. The latter is called *chloroxalic ether*. It is a crystallisable solid, fusible at 288°. Dry ammonia acts on it as on oxalic ether, producing *chloroxamethane*, a crystalline compound analogous to oxamethane. It was formerly stated that oxamethane, $C_8 H_7 N O_6$, has the composition of oxamate of oxide of ethyle $(C_4 H_5) O + C_4 H_2 N O_5$; or of oxalic ether *plus* oxamide $(C_4 H_5) O, C_2 O_3 + N H_2, C_2 O_2$. In like manner, chloroxamethane represents chloroxalic ether *plus* oxamide: $(C_4 Cl_5) O, C_2 O_3 + N H_2, C_2 O_2 = C_8 H_2 Cl_5 N O_6$. When chloroxamethane is left in contact with ammonia, it takes up 2 eq. of water, and forms a new salt, chloroxalovinate of ammonia, $C_4 Cl_5 O, N H_4 O, 2 C_2 O_3$, which is very deliquescent. From the corresponding salt of soda the chloroxalovinic acid may be obtained, which may of course be viewed as an acid oxalate of the compound $C_4 Cl_5 O$. Its formula is, $C_4 Cl_5 O, C_2 O_3 + H O, C_2 O_3$. By the action of alcohol on chloroxalic ether, there is formed a neutral oil, $C_8 Cl_5 O_7$, which contains the elements of anhydrous chloroxalovinic acid, $C_4 Cl_5 O, 2 C_2 O_3$; and when dissolved in potash, yields chloroxalovinate of potash.

Carbonic ether, by the action of chlorine, yields two products: 1st. Bichloruretted carbonic ether, $C_4 \left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right. O, CO_2 = C_5 H_3 Cl_2 O_3$; and 2nd. Perchloruretted carbonic ether, $C_4 Cl_5 O, C O_2 = C_5 Cl_5 O_3$. The former is an oily liquid ; the latter crystallisable.

Chloride of ethyle $(C_4 H_5)$ Cl, when acted on by chlorine, yields a very remarkable series of products, in which the hydrogen is gradually replaced by chlorine, as mentioned at p. 374, to which I refer for the formulæ. I shall only here mention, that the compound there represented as $C_4 \left\{\begin{matrix} H_4 \\ Cl \end{matrix}\right., Cl, = C_4 H_4 Cl_2$, corresponds to aldehyde, and is, therefore, probably $(C_4 H_3) Cl + H Cl$, just as aldehyde is $(C_4 H_3), O + H O$. In like manner, the compound $C_4 \left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right., Cl = C_4 H_3 Cl_3$, corresponds to dry acetic acid, $C_4 H_3 O_3$. The action of potash on these two compounds confirms this view, according to which they are protochloride and perchloride of acetyle.

When *alcohol*, the hydrated oxide of ethyle, is subjected to the long-continued action of chlorine, aided by the sun's rays, there is formed, after a very tedious operation, a remarkable compound called *chloral*, the empirical formula of which is $C_4 H Cl_3 O_2 = C_4 Cl_3 O + H O$. This compound represents aldehyde or hydrated oxide of acetyle, in which the hydrogen of the acetyle has been replaced by chlorine. It is an oily liquid, boiling at 199°, of Sp. G. 1·502. Like aldehyde, chloral, when kept, is spontaneously converted into an insoluble solid compound, which has the same composition as chloral itself. In contact with water, chloral is soon converted into a solid hydrate, which dissolves in a larger quantity of water. It contains 1 eq. chloral and 2 eq. water. When heated with caustic alkalies, chloral produces formiate of the alkali and perchloride of formyle, $C_4 H Cl_3 O_2 + HO, KO = (C_2 H) O_3, KO + (C_2 H) Cl_3$. The perchloride of formyle, in contact with the alkali, is partly decomposed, yielding chloride of the metal.

Pure Acetic Acid, when acted on by chlorine and the sun's rays, is converted into a crystallisable acid, the chloracetic acid, $C_4 Cl_3 O_3, HO$. As acetic acid may be considered to be aldehyde *plus* 2 eq. oxygen, or hydrated peroxide of acetyle, so chloracetic acid is chloral *plus* 2 eq. oxygen, or hydrated peroxide of $C_4 Cl_3$, which may be called *chloracetyle*. Chloracetic acid forms tabular crystals, fusible at 113°, boiling at 390°. The density of the liquefied acid at 113° is 1·617. When heated with excess of potash, it yields first carbonic acid and perchloride of formyle, $C_4 Cl_3 O_3, HO + 2 KO = 2 (KO, CO_2) + C_2 HCl_3$. The perchloride of formyle is partly converted by another portion of potash, into formiate of potash and chloride of potassium. $C_2 HCl_3 + 4 KO = 3 K Cl + KO, C_2 HO_3$.

With bases, chloracetic acid forms salts which are very analogous to the acetates; and it is very important here to observe, that both in chloral and chloracetic acid, the substitution of chlorine for all the hydrogen of the radical (acetyle) of aldehyde and acetic acid, has not affected the general chemical characters of the compounds; that, in other words, the original type has been retained. We have also seen, in the preceding pages, among the products of the action of chlorine on oxide of ethyle and on the salts of oxide of ethyle, that oxide of ethyle, $C_4 H_5 O$, is converted into oxide of chlorethyle, $C_4 Cl_5 O$, without the type being altered: the oxide of chlorethyle forming with the acids previously combined with oxide of ethyle, compounds perfectly analogous to the ethers from which they are obtained.

The *sulphuret of ethyle* is readily acted on by chlorine, and yields a yellow oily liquid, of Sp. G. 1·673, boiling at 320°, of a most fetid odour, the formula of which is $C_4 \left\{ \begin{matrix} H \\ Cl_4 \end{matrix} \right. S$. Here 4 eq. of hydrogen of the compound, $C_4 H_5 S$, are replaced by chlorine.

Heavy muriatic ether is an oily liquid, formed by the action of moist chlorine on alcohol. It is obviously a mixture, and probably contains aldehyde, chloride of ethyle, chloral, and products intermediate between aldehyde and chloral.

Bromal. $C_4 Br_3 O, HO$. This compound, analogous to chloral, is formed by the action of bromine on alcohol. It forms a hydrate with 3 eq. water. By caustic alkalies it is resolved into formic acid, which combines with the alkali, and perbromide of formyle.

Iodine does not, so far as is known, produce a compound corresponding to chloral and bromal; but a solution of iodine in alcohol, treated with an alcoholic solution of potash, yields formiate of potash and peroxide of formyle, $C_2 H I_3$.

By the action of chlorine on alcohol, holding in solution hydrocyanic acid on a metallic cyanide, there is produced a crystalline compound, the empirical formula of which appears to be $C_{16} H_{14} N_2 Cl_2 O_8$. This is equal to 3 eq. aldehyde, 2 eq. chloride of cyanogen, and 2 eq. water; but the true nature of this compound is unknown.

3. Compounds derived from Alcohol, but of uncertain constitution.

Olefiant Gas. Syn. *Hyduret of Acetyle.* $C_4 H_4 = C_4 H_3, Cl = Ac H$. This well-known compound is generally present in coal gas, oil gas, and in general, in all gaseous mixtures produced by the action of heat on organic substances. It is best obtained pure by heating 1 part of alcohol with 6 or 7 of oil of vitriol. There is produced some ether, then sweet oil of wine, and lastly, a mixture of sulphurous acid and olefiant gases. By passing the gas through milk of lime, the sulphurous acid is removed, and by then passing it through oil of vitriol, the ether, alcohol, and water which may be present, are likewise separated. Pure olefiant gas has been already described (see p. 121, Part I); here we shall attend to its combinations. It is absorbed by anhydrous sulphuric acid, forming the crystalline compound formerly mentioned, $2\, S O_3 + C_4 H_4$, which, in contact with water, produces ethionic acid. When mixed with its own volume of chlorine, both gases are condensed into a liquid, the composition of which is $C_4 H_4 Cl_2$. This is the oily compound, from which the gas was called olefiant gas: the oil is often called the oil of the Dutch chemists; having been discovered by an association of chemists in Holland.

When mixed with 2 vol. of chlorine, and set fire to, the whole of the carbon of the gas is deposited in the solid form or as smoke, while all the hydrogen forms hydrochloric acid, $C_4 H_4 + Cl_4 = 4\, H Cl + C_4$.

The oil of olefiant gas, or of the Dutch chemists, $C_4 H_4, Cl_2$, may be viewed as composed of hydrochloric acid, and a chloride of acetyle; $H Cl + C_4 H_3 Cl$. When acted on by an alcoholic solution of potash, chloride of potassium and water are formed, and a new compound separates, which is the *protochloride of acetyle*, $C_4 H_3 Cl$. It is gaseous at ordinary temperatures, has an alliaceous smell, and burns, like all similar chlorinised compounds, with a dark red flame edged with green. At 0° it condenses into a liquid.

When this protochloride of acetyle is acted on by perchloride of antimony, it yields, among other products, a liquid, boiling at 240°, which is $C_4 H_3 Cl_3$, and therefore has the same composition as perchloride of acetyle, formerly mentioned. But the action of potash, dissolved in alcohol, proves that these two compounds are distinct, and that the one now under consideration is $C_4 H_2 Cl_2 + HCl$. At all events, it yields chloride of potassium, water, and a very volatile liquid, $C_4 H_2 Cl_2 = 2 (C_2 H, Cl)$, or in other words, protochloride of formyle.

By continuing the action of chlorine there is obtained a compound $C_4 H_2 Cl_4, = C_4 HCl_3 + HCl$; which, with potash, yields the body $C_4 HCl_3$; and the final result of this action is the protochloride of carbon, $C_4 Cl_4 = 4 CCl$; which, however, unites with chlorine to produce the sesquichloride, $C_4 Cl_4 + Cl_2 = C_4 Cl_6 = 2 C_2 Cl_3$.

The *perchloride of acetyle* has been already mentioned as a product of the action of chlorine on ether: it is $C_4 H_3 Cl_3 = AcCl_3$.

The oil of olefiant gas, $C_4 H_4 Cl_2$, which may be considered the hydrochlorate of chloride of acetyle, $C_4 H_3, Cl + HCl$, is best prepared by passing olefiant gas into perchloride of antimony, as long as it is absorbed. The mixture, if distilled, yields the oil in question. It is purified by alternate distillation with water and sulphuric acid, and finally drying it with chloride of calcium. It is a very mobile liquid, of a pleasant etherial smell, and a very sweet taste; it boils at 180°, is insoluble in water, soluble in alcohol and ether.

When subjected to the action of chlorine, it yields hydrochloric acid, and products rich in chlorine. Among these are, the hydrochlorate of chloride of formyle, $C_2 H Cl + HCl$, which distils at 240°, and the bichloride of formyle, $C_2 H, Cl_2$, which distils at 275°. This last is finally converted into sesquichloride of carbon; for $C_2 H, Cl_2 + Cl_2 = C_2 Cl_3 + HCl$.

Chloretheral is the name given by D'Arcet to a compound formed by the action of chlorine on olefiant gas, containing both alcohol and ether. Its empirical formula is $C_4 H_4 Cl O$; so that it may be aldehyde, *plus* oil of olefiant gas; $C_4 H_3 O, HO + C_4 H_3 Cl, H Cl = 2 (C_4 H_4 Cl O)$; or oxychloride of acetyle, *plus* oxide of ethyle: $C_4 H_3 \left\{ \begin{matrix} O \\ Cl_2 \end{matrix} \right. + C_4 H_5 O = 2 (C_4 H_4 Cl O)$. The true nature of this compound is unknown.

Bromine forms, with olefiant gas, a liquid compound analogous to the oil of olefiant gas. Its formula is $C_4 H_3, Br + H Br$.

Iodine forms, with olefiant gas, a solid compound, which would appear to be $C_4\ H_3, H + I_2$ rather than $C_4\ H_3, I + H I$.

Anhydrous sulphuric acid absorbs olefiant gas, producing a white crystalline solid, $2\ S O_3 + C_4\ H_4\ H_4$; which, when dissolved in water, forms with 1 eq. of water, ethionic acid, $2\ S O_3 + C_4\ H_5\ O = C_4\ H_5\ O_2 + S_2\ O_5$. The original crystalline compound has been called sulphacetylic acid.

4. Action of bichloride of platinum on Alcohol.

This action is very complex, yielding aldehyde, chloride of ethyle, chloride of acetyle, and other volatile compounds, along with a salt, composed of chloride of platinum and chloride of acetyle. It is possible that 3 eq. of oxide of ethyle, with 4 eq. of bichloride of platinum, may yield 1 eq. aldehyde, 1 eq. water, 4 eq. hydrochloric acid, and 2 eq. of the new salt. $3\ (C_4\ H_5\ O) + 4\ Pt\ Cl_2 = C\ \ H_3\ O, H O + H O + 4\ H Cl + 2\ (C_4\ H_3\ Cl + Pt_2\ Cl)$. Zeise considers the salt to be $C_4\ H_4 + 2\ Pt\ Cl$, which formula differs from the preceding in containing 1 eq. hydrogen more. Malaguti supposes it to be $C_4\ H_3\ O + 2\ Pt\ Cl$; but Zeise has shown that it contains no oxygen. It does not crystallise, but forms a gummy mass, spontaneously decomposing when kept.

When a solution of bichloride of platinum in alcohol is digested with a little hydrochloric acid, and chloride of potassium, the alcohol distilled off, and the residue neutralised by carbonate of potash, a yellow crystallisable salt is obtained, which contains the preceding compound, plus 1 eq. chloride of potassium, $C_4\ H_3\ Cl + Pt_2\ Cl + K\ Cl$. Similar double salts are formed with chloride of sodium and chloride of ammonium.

These double salts form with ammonia a yellow precipitate, which is $C_4\ H_3\ Cl, Pt\ Cl + N H_3$.

5. Action of heat on acetic acid and the acetates.

Acetone. Syn. *Pyroacetic Spirit. Mesitic Alcohol.* Formula $C_3\ H_3\ O$. Is formed when acetic acid is passed through a tube heated to low redness, along with carbonic acid, carbonic oxide, and carburetted hydrogen : also when the acetate of an alkali or alkaline earth is exposed to heat, when a carbonate is left, and acetone distils over. It is best prepared by distilling a mixture of 2 parts of crystallised acetate of lead, and 1 part quicklime. Its formation is easily explained ; for anhydrous acetic acid, $C_4\ H_3\ O_3$ contains the elements of 1 eq. carbonic acid, and 1 eq. acetone. $C_4\ H_3\ O_3 = C O_2 + C_3\ H_3\ O$. Acetone is also formed in the distillation of sugar, of citric acid, of tartaric acid, &c. It is purified by rectification, until its boiling point becomes constant, at 100°. It is a clear and colourless liquid, of Sp. G. 0·7921, and has a peculiar smell and a pungent taste. It is miscible with water, alcohol, and ether, in all proportions; and is separated from water by the addition of caustic potash, chloride of calcium, or other salts insoluble in acetone.

Heated with hypochlorite of lime, it is converted into carbonic acid and perchloride of formyle. When prepared by the distillation of acetates, acetone is accompanied by an oily liquid $C_{10} H_8 O$.

Acetone contains, in 3 eq., the elements of 1 eq. carbonic ether and 1 eq. olefiant gas (hyduret of acetyle). $C_4 H_5 O, CO_2 + C_4 H_3, H = C_9 H_9 O_3 = 3 (C_3 H_3 O)$; or, in 4 eq.: we have the elements of 1 eq. acetic ether, and 1 eq. hyduret of acetyle: $C_4 H_5 O, C_4 H_3 O_3 + C_4 H_3, H = C_{12} H_{12} O_4 = 4 (C_3 H_3 O)$. Kane considers acetone to be $C_6 H_6 O_2 = C_6 H_5 O, H O$; that is, the hydrated oxide of a radical $C_6 H_5$, which he calls *mesityle*. In this view, acetone is analogous to alcohol, and $C_6 H_5 O$, the oxide of mesityle, to ether. But although Kane has obtained this compound $C_6 H_5 O$, and also another $C_6 H_5 Cl$, his chloride of mesityle, and although he has likewise formed double salts containing sulphuric acid and the elements $C_6 H_5 O$, yet the analogy is far from being established. It has not yet been found possible to reproduce acetone, the *alcohol*, from the supposed *ether* of the series, as we can reproduce alcohol from the salts of oxide of ethyle. Moreover, in these double salts, the body $C_6 H_5 O$, does not act as a base, but is only coupled with the acid, as naphthaline in sulphonaphthalic acid. We shall not, therefore, enter into minute details of the theoretical views alluded to. It is sufficient to enumerate the supposed radical *mesityle*, $C_6 H_5$; its oxide $C_6 H_5 O$, oxide of mesityle; its hydrated oxide, $C_6 H_5 O, H O$ (acetone); the chloride and iodide of mesityle, $C_6 H_5 Cl$ and $C_6 H_5 I$; the acid sulphate of oxide of mesityle, $C_6 H_5 O, H O, 2 S O_3$ (sulphomesitylic acid); the double salts of this sulphate, the formula of which is $C_6 H_5 O, H O, 2 M O, 2 S O_3$; and a compound discovered by Zeise, containing oxide of mesityle with chloride of platinum, $C_6 H_5 O, Pt Cl$.

The action of nitric acid on acetone gives rise to a new product: *nitrite of oxide of pteleyle*, $C_6 H_3 O, N O_3$; phosphoric acid appears to form a compound acid with acetone; and when phosphorus, iodine, and acetone are distilled together, another acid is obtained, which appears to contain hypophosphorous acid.

When chlorine acts on acetone, it produces a liquid, $C_6 H_4 Cl_2 O_2$, which is called *mesitic chloral*.

Mesitylene, $C_6 H_4$. This compound is obtained when acetone is distilled with fuming sulphuric acid. It is an oily liquid, boiling about 300°. Acetone $2 (C_3 H_3 O) = C_6 H_4 + 2 HO$; and this explains its production.

When mesitylene is acted on by nitric acid, it yields a liquid $C_6 H_4 O_2$, called by Kane mesitic aldehyde. But when chlorine is passed through mesitylene, a crystalline solid is obtained, containing a new radical, pteleyle, combined with chlorine. $C_6 H_4 + Cl_2 = C_6 H_3 Cl + H Cl$. The compound $C_6 H_3 Cl$ is the chloride of the supposed new radical pteleyle, $C_6 H_3$. Kane has described a compound in yellow scales, which he considers to be iodide of pteleyle. It is very desirable that the whole of the compounds derived from acetone should be again carefully examined, since their true constitution cannot be considered as established.

COMPOUNDS CONTAINING ARSENIC, DERIVED FROM ACETYLE.

When acetate of potash is heated along with arsenious acid, a very remarkable liquid is obtained, which is the oxide of a new radical. This liquid, which is spontaneously inflammable, and has a most offensive alliaceous smell, has been long known in an impure state, under the names of the liquor of Cadet, and *alcarsine*. Bunsen, by a long series of the most profound and persevering researches, established its true character as the oxide of the radical *kakodyle*. He has even succeeded in obtaining the radical itself in the separate state, and in establishing the most perfect analogy between that radical and a metal, in all its chemical relations.

XVIII. KAKODYLE. $C_4 H_6 As_2 = Kd$.

The radical is best obtained from the chloride of kakodyle, Kd Cl, by the action of zinc at 212°. Chloride of zinc is formed, and kakodyle is set free. It is rectified in an apparatus filled with carbonic acid gas, to prevent decomposition. It is a clear liquid, refracting light strongly. When cooled, it crystallises in large square prisms, and acquires, when pure, the appearance of ice. Its smell is insupportably offensive, and its vapour is highly poisonous. The two latter characters belong to all the compounds of kakodyle, with hardly an exception. Kakodyle is spontaneously inflammable in the air: a rod moistened with it instantly takes fire when exposed to the air. It forms two distinct oxides: the protoxide Kd O (alkarsine), and kakodylic acid, $Kd O_3$.

Protoxide of Kakodyle. $C_4 H_6 As_2, O = Kd O$.

SYN. *Alkarsine.* This is the chief ingredient of the liquor of Cadet; it is purified by repeated rectifications in an atmosphere of carbonic acid, and is, when pure, a limpid etherial liquid, refracting light powerfully; it boils at about 300°, and at —9° it crystallises in white scales of a satiny lustre. Its smell is most offensive, and its taste very nauseous. If placed on the skin, it causes violent itching, and if taken internally it is a most energetic poison. It is sparingly soluble in water, more soluble in alcohol and ether. Like kakodyle, it takes fire when exposed to the air. When left under water, it gradually disappears, being for the most part converted into kakodylic acid. The production of oxide of kakodyle is very simple: 2 eq. dry acetic acid and 1 eq. arsenious acid yield 4 eq. carbonic acid and 1 eq. oxide of kakodyle. $2\,(C_4\,H_3\,O_3) + As_2\,O_3 = 4\,CO_2 + C_4\,H_6\,As_2\,O$.

Kakodylic Acid. $Kd\,O_3 = C_4\,H_6\,As_2, O_3$.

Syn. *Alcargene.* Formed by the gradual oxidation of the protoxide, under water. It forms oblique four-sided prisms, brittle, and of a glassy lustre. They have no smell, and are soluble in water and alcohol. Its salts do not crystallise. Many reducing agents convert it into the protoxide by removing 2 eq. of oxygen. It is not in the least poisonous.

There appears to be an intermediate oxide $Kd\,O_2$; but it has not been obtained in a state of purity.

Chloride of Kakodyle, $Kd\,Cl = C_4\,H_6\,As_2, Cl_4 = Kd\,Cl$, is obtained by heating a compound of oxide of kakodyle and corrosive sublimate along with hydrochloric acid: $Kd\,O, Hg\,Cl_2 + H\,Cl = Kd\,Cl + H\,O + Hg\,Cl_2$. It is a volatile horribly fetid liquid, the vapour of which attacks strongly the lining membrane of the nose, and provokes a flow of tears. When exposed to the air it deposits crystals of an oxychloride of kakodyle $Kd\,O + 3\,Kd\,Cl$. The iodide, bromide, and fluoride of kakodyle are in all points analogous to the chloride; and form, when exposed to the air, oxyiodide, oxybromide, &c.

Sulphur forms with kakodyle three compounds; the *protosulphuret,* $Kd\,S$, is obtained by distilling chloride of kakodyle with hydrosulphuret of sulphur of barium: $Kd\,Cl + Ba\,S, HS = Kd\,S + Ba\,Cl + HS$. It is a clear, volatile, very fetid liquid, heavier than water. It dissolves sulphur, forming the *bisulphuret* $Kd\,S_2$, which is a very permanent compound. The *persulphuret,* $Kd\,S_3$ is a sulphur acid, and forms sulphur salts which are very permanent, with the sulphurets of highly basic metals. The sulphur salt of kakodyle and lead, $Pb\,S, Kd\,S_3$ crystallises beautifully.

Cyanide of Kakodyle, $Kd\,Cy = C_4\,H_6\,As_2, C_2\,N$, is formed by distilling bicyanide of mercury with water and oxide of kakodyle. When pure it forms large brilliant crystals, very fusible and volatile. The vapour of this compound is so poisonous as to be in the highest degree dangerous to the experimenter.

COMPOUNDS OF KAKODYLE CONTAINING PLATINUM.

Chloride of Kakoplatyle, $C_4\ H_7\ As_2\ PtO_2$, Cl. This compound is formed when an alcoholic solution of bichloride of platinum is added to a similar solution of chloride of kakodyle, when a reddish brown precipitate is formed, which, being boiled with water, gives a solution from which on cooling, needles of the new compound are deposited. *Bromide of kakoplatyle* and *iodide of kakoplatyle* may be formed from the chloride, and are analogous to it. The former appears in large yellow crystals, the latter in golden micaceous scales.

When the chloride is acted on by sulphate of silver, there is obtained, along with chloride of silver, the sulphate of the oxide of kakoplatyle, $C_4\ H_7\ As_2\ Pt\ O_3,\ SO_3$. It forms white crystalline grains.

The radical of these singular compounds, kakoplatyle, may be represented as composed of protoxide of platinum, water, and kakodyle; $PtO,\ HO,\ C_4\ H_6\ As_2$. We have, therefore, the following series, which, like those derived from the bases containing platinum formerly described, throws much light on the nature of the vegetable bases.

Radical, Kakoplatyle	$Pt\ O + Kd \quad = \quad C_{14}\ H_6\ As_2\ Pt\ O.$
Chloride of do., anhydrous	$Pt\ O,\ Kd + Cl$
Chloride, hydrated	$Pt\ O,\ Kd + Cl + H\ O$
Chloride, ammoniated	$Pt\ O,\ Kd + Cl + NH_3$
Oxide, hydrated	$Pt\ O,\ Kd + O\ + H\ O$
Sulphate, hydrated	$(Pt\ O,\ Kd + O,\ H\ O) + S\ O_3.$

It is to be particularly borne in mind that this radical, whose basic character is quite obvious, contains two metals, arsenic and platinum, quite foreign, in general, to organic compounds.

The existence of kakodyle itself, and the perfect analogy which may be traced between it and the simple metals, in their relations to all other substances, render the results of the researches of Bunsen, which have been so very briefly described in this work, of the very highest importance to the theory of organic compounds, and especially to that of compound radicals.

APPENDIX TO ETHYLE AND ACETYLE.—SUGAR.

Sugar, as the substance from which alcohol and all the compounds of ethyle are exclusively obtained, comes properly to be considered here as an appendix to these compounds. There are several kinds of sugar, capable of undergoing fermentation and of producing alcohol. These are, cane sugar; grape sugar; (sugar of starch; of honey; diabetic sugar); sugar of milk; and uncrystallisable sugar. The sugar of mushrooms has been found to be mannite, which is not fermentescible.

1. *Cane sugar*, $C_{12} H_9 O_9 + 2 HO$, occurs in great abundance in the sugar cane, the beet root, the maple, besides many other vegetables. It is extracted from the juice of these plants by crystallisation, the evaporation being conducted at as low a temperature as possible. It crystallises with great facility, either in small grains by rapid cooling of a strong syrup, as in loaf sugar; or in large distinct crystals by a slow process, as in sugar candy. The above formula represents the composition of pure crystallised sugar.

Sugar forms large transparent hard crystals, which melt at 302°, or according to Peligot at 356°, forming a viscid liquid, which on cooling forms a transparent amorphous mass, *barley sugar*. This, when kept, gradually becomes crystalline, opaque and friable. About 420° sugar is converted into caramel, losing 3 eq. of water.

Sugar dissolves in $\frac{1}{3}$ of its weight of cold, and in any quantity of boiling water; a solution saturated at 230° becomes a solid crystalline mass on cooling (tablet): a solution saturated in the cold is viscid, and is called syrup. Syrup, when long boiled loses the property of crystallising. The crystallisation of sugar from syrup is also prevented by the addition of $\frac{1}{20}$ of oxalic, citric, or malic acids. When boiled with diluted sulphuric acid, cane sugar is converted into grape sugar. With strong sulphuric acid it produces a dark brown liquid, containing a new acid, sulphosaccharic acid. Nitric acid converts it into saccharic acid, oxalic acid, and carbonic acid.

When boiled with very diluted sulphuric acid, sugar absorbs oxygen from the air, and produces formic acid, and a brown matter identical with ulmine, formed by the decay of wood. Sugar prevents the precipitation of many metallic solutions by alkalies; and when mixed with oxide of copper and potash, the oxide of copper is dissolved, forming a purple solution, which on boiling, deposits red suboxide of copper. It reduces partially the oxides of many metals, when boiled with their solutions.

Sugar forms crystallisable compounds with the alkalies, oxide of lead, and chloride of sodium. When in contact with the lining membrane of the stomach of a calf, or with the caseine of milk, sugar is transformed into lactic acid.

Sugar, if taken along with nitrogenised food, may be called nutritious: it would appear, however, to act chiefly in contributing to the support of respiration, and thus keeping up the animal heat. An animal, confined to sugar as food, soon dies from want of nitrogen, with the symptoms of starvation.

When a solution of sugar is examined by polarised light, it gives rise to a series of rings of the prismatic colours, when the plane of polarisation is made to rotate from left to right.

SUGAR WITH BASES AND SALTS.

With lime sugar forms a sparingly soluble compound, $C_{12}H_9O_9 + \left\{\begin{matrix}CaO\\HO\end{matrix}\right.$. With baryta, it forms a crystallisable compound, $C_{12}H_9O_9 \left\{\begin{matrix}BaO\\HO\end{matrix}\right.$. With oxide of lead it yields an insoluble compound, $C_{12}H_9O_9$, 2 PbO; and with common salt it yields a crystalline compound, $2\,C_{12}H_9O_9 + \left\{\begin{matrix}3\,HO\\NaCl.\end{matrix}\right.$

2. *Grape Sugar.* Syn. *Glucose. Diabetic Sugar. Starch-Sugar,* $C_{12}H_{14}O_{14}$. This sugar occurs in the juice of many fruits, and is besides a product of the metamorphoses of starch, cane sugar, woody fibre, sugar of milk, &c., when boiled with diluted acids. It may also be obtained from starch by the action of infusion of malt, or of diastase. It occurs in the urine of those affected with *diabetes mellitus.* The crystals which form in honey are likewise grape sugar.

It is best extracted from *dried grapes,* or honey, and is also prepared on the large scale from starch. 1 part of starch is boiled with 4 of water, and from $\frac{1}{100}$ to $\frac{1}{10}$ of sulphuric acid, during 36 or 40 hours; or an infusion of malt is added to jelly of starch, which soon becomes liquid, and, in a few hours, is converted into sugar. When acid is used, it is neutralised by chalk, the solution of sugar filtered, and evaporated to a syrup, or, if required, to a dry mass. In this process, starch, $C_{12}H_{10}O_{10}$, takes up 4 eq. water, and produces grape sugar $C_{12}H_{14}O_{14}$; so that 100 parts of pure starch yield, or ought to yield, 122 of grape sugar. The same explanation, only varying the quantity of water, applies to the conversion into grape sugar of cane sugar, $C_{12}H_{11}O_{11}$; woody fibre, $C_{12}H_8O_8$; and sugar of milk $C_{12}H_{12}O_{12}$, these compounds requiring 3, 6, and 2 eq. of water respectively to form grape sugar.

The action of infusion of malt is not explained: all that we know is, that this infusion, or a solution of diastase, a substance contained in it, do actually cause starch to take the form of grape sugar. It is probable that the diastase is in a state of decomposition, and may act as a ferment. The action of the acid would seem to be equally obscure; but there is some reason to think that there is first formed, as in the case of ether, a coupled acid, or acid salt, which like sulphovinic acid, is decomposed by boiling. According to De Saussure, sulphuric acid and starch actually form a crystallisable compound.

Grape sugar crystallizes from alcohol in square tables or cubes: a concentrated syrup of it yields only a mass formed of crystalline grains. It is much less soluble, requiring 1½ part of cold water, and less sweet to the taste than cane sugar: in fact 1 part of cane sugar sweetens as much as 2½ of grape sugar. It is much more soluble in cold alcohol than cane sugar. At 212° grape sugar loses 2 eq. of water; when heated beyond 284° it becomes caramel. Hot water dissolves any quantity of grape sugar, but the syrup is not nearly so viscid as that of cane sugar. Solution of grape sugar exhibits the prismatic rays with polarised light when the plane of polarisation is rotated from right to left, the colours being less brilliant. Now, as cane sugar, when fermenting, becomes first grape sugar, the coloured rings at first shown by it when the plane of polarisation rotated from left to right disappear during fermentation; but reappear when rotation is made from right to left.

Grape sugar is easily distinguished from cane sugar by the action of acids and bases. Strong sulphuric acid dissolves without charring it, forming sulphosaccharic acid; and the alkalies or alkaline earths, which do not decompose cane sugar unless very concentrated, rapidly convert grape sugar into a brown matter. Peroxide of lead converts it, at 212°, into basic formiate of lead, carbonate of lead, and water.

With baryta and lime, and oxide of lead, grape sugar forms compounds which it is difficult to obtain pure. That with baryta appears to contain 3 eq. baryta for 2 eq. of sugar, and as the baryta replaces water in such compounds, it is probably $C_{24} H_{25} O_{25}, 3\ BaO = C_{24} H_{22} O_{22} \left\{\begin{array}{l} 3\ BaO \\ 3\ HO \end{array}\right.$. The compound with lime appears to be $C_{12} H_{12} O_{12}, 2\ CaO$; and that with lead, $C_{2} H_{11} O_{11}, 3\ PbO$. If we suppose the dry grape sugar to be $C_{12} H_{11} O_{11}$, and to combine with 3 eq. water and 3 eq. base, then we should have

Crystallised grape sugar	$C_{12} H_{11} O_{11} + 3\ HO$
Compound with baryta	$\left\{\begin{array}{l} C_{12} H_{11} O_{11} + 3\ HO \\ C_{12} H_{11} O_{11} + 3\ BaO \end{array}\right.$
———— lime	$C_{12} H_{11} O_{11} + \left\{\begin{array}{l} 2\ CaO \\ HO \end{array}\right.$
———— oxide of lead . . .	$C_{12} H_{11} O_{11} + 3\ PbO$

But the compound which grape sugar forms with common salt, and which crystallises very readily, does not agree exactly with this view. The crystals are $2\ (C_{12}\ H_{12}\ O_{12})+NaCl+2\ HO$; and at 212° they lose the two equivalents of water.

The sulphosaccharic acid, above mentioned, as being formed when grape sugar is acted on by oil of vitriol, has not been fully examined. It forms a soluble salt with baryta.

With organic acids grape sugar forms compounds, the sugar in which cannot be brought to crystallise. Hence organic acids in vegetable juices act injuriously by first converting cane sugar into grape sugar, and then forming with it uncrystallisable compounds.

When sugar is boiled with hydrochloric acid, it yields different brown products, according to the strength of the acid. With equal parts of acid and water, it yields a body, $C_{24}\ H_{11}\ O_9$: with a weaker acid, two brown compounds; a soluble one, $C_{40}\ H_{14}\ O_{12}$, and an insoluble one, $C_{40}\ H_{16}\ O_{14}$. When boiled with diluted sulphuric acid two substances are formed, which are nearly black; one, sacchulmine, insoluble, and the other sacchulmic acid, soluble in ammonia. The latter is $C_{35}\ H_{10}\ O_{15}$.

When boiled with alkalies, cane sugar is first converted into grape sugar, and then into formic acid, and two new acids, the glucic acid and the melassic acid. Glucic acid is very soluble, and its formula is either $C_{24}\ H_{15}\ O_{15}, 6\ HO$, or $C_{12}\ H_8\ O_8, 3\ HO$. It is chiefly formed before the application of heat, which converts it into melassic acid. This latter acid is formed from sugar by the joint action of heat and alkalies. It has a very dark colour, and when separated by hydrochloric acid, appears as a black flocculent deposit. Its formula is $C_{24}\ H_{12}\ O_{10}$ (?).

Caramel, the black matter formed by heating sugar to about 400°, has the formula of anhydrous cane sugar, $C_{12}\ H_9\ O_9$. It dissolves readily in water forming a solution like sepia, which is tasteless when pure. The caramel of commerce contains a good deal of undecomposed sugar.

When sugar is distilled with 3 parts of lime, it yields a liquid which is a mixture of acetone and metacetone. Metacetone is a colourless liquid, of an agreeable odour, boiling at 183°, and insoluble in water. Its formula is $C_6\ H_5\ O$; and it may be considered as 2 eq. acetone $C_6\ H_6\ O_2$, *minus* 1 eq. water.

1 eq. of anhydrous sugar	C_{12}	H_9	O_9
Contains—1 eq. acetone	C_3	H_3	O
1 eq. metacetone	C_6	H_5	O
3 eq. carbonic acid	C_3		O_6
1 eq. water		H	O
Together	C_{12}	H_9	O_9

The formation of these products is therefore easily accounted for.

When sugar is heated with hydrate of potash, several products are formed, but among them is an acid, $C_6\,H_5\,O_3, HO$, which is metacetonic acid, evidently derived from metacetone by oxidation at the expense of the hydrate. It is very similar to acetic acid.

ACTION OF NITRIC ACID ON SUGAR.

Saccharic Acid, $C_{12}\,H_{10}\,O_{11}, 5\,HO$?, or $C_6\,H_4\,O_7, HO$, is one of the products of the action of diluted nitric acid on cane or grape sugar. When stronger acid is used, oxalic and carbonic acids are the chief products. When sugar has been heated with 2 parts of nitric acid and 10 of water, the acid liquid gives, with basic acetate of lead, an insoluble saccharate of lead, which is decomposed by sulphuretted hydrogen, and the acid solution so far neutralised with potash that on evaporation it yields crystals of the acid saccharate of potash. This salt is purified, again converted into saccharate of lead, and again the lead salt is decomposed by sulphuretted hydrogen. The acid this time is pure. It crystallises with difficulty.

This acid has been supposed to be quintibasic, and to form 5 series of salts, but the latest researches of Heintz lead to the conclusion that it is either $C_6\,H_4\,O_7, HO$, or $C_{12}\,H_8\,O_{14}, 2\,HO$. Owing to the very discordant results of different experimenters, we shall not here enter into details which are uncertain. Saccharic acid forms a crystallisable acid salt with potash, and definite salts with many other bases. It is isomeric with mucic acid: for $C_{12}\,H_8\,O_{14}, 2\,HO$ is the probable formula of mucic acid.

The saccharate of silver, when gently heated under water, is decomposed, the silver being reduced; and as this occurs without effervescence, the reduced metal adheres to the glass, and forms a bright mirror surface. The other saccharates are only interesting in respect to their composition. On the whole, saccharic acid is a compound of high theoretical interest, and the formation of two isomeric acids, saccharic and mucic, by the action of nitric acid on cane and grape sugar on the one hand, and on sugar of milk on the other, is a fact which may hereafter lead to a knowledge of the true constitution of the different kinds of sugar.

Notwithstanding the fact that cane sugar is easily converted into grape sugar, and that the formulæ differ only by 3 eq. water, it is evident that these two kinds of sugar differ more than if they were merely different hydrates of the same compound. Strong mineral acids instantly decompose cane sugar, but have little action on grape sugar; while alkalies, which combine with cane sugar to form crystalline compounds, rapidly convert grape sugar into dark compounds, glucic and melassic acids. And although both sugars agree in undergoing the same (vinous) fermentation, yet it is most probable that cane sugar, before fermenting, becomes grape sugar.

When vegetable juices containing cane sugar are evaporated, the presence of organic acids causes its conversion into grape sugar; and when lime is added, to clarify the juice, the action of the lime on grape sugar when evaporated, produces glucic and melassic acids; in other words, renders much sugar dark and uncrystallisable, converting it into molasses. A great part of the loss owing to this cause has of late years been avoided by carefully neutralising with sulphuric acid as soon as the lime has effected the clarification.

3. *Sugar of milk, or lactine*, $C_{24} H_{19} O_{19} + 5\ HO = C_{24} H_{24} O_{24}$, is obtained by evaporating clarified whey till it crystallises. When pure it forms hard white crystals, soluble in 5 or 6 parts of cold and 2½ of hot water. The taste of the crystals is feeble, but a concentrated solution tastes very sweet. It is insoluble in ether and alcohol. It stands between cane sugar and grape sugar in composition; for while cane sugar is $C_{12} H_{11} O_{11}$, and grape sugar $C_{12} H_{14} O_{14}$, lactine is $C_{24} H_{24} O_{24} = 2\ (C_{12} H_{12} O_{12})$. By boiling with diluted acids, it is converted into grape sugar. By the action of nitric acid, it yields *mucic* or *saccholactic acid.* It combines with ammonia and with oxide of lead. Its presence prevents the precipitation of many metallic solutions. Sugar of milk is susceptible of the vinous fermentation, and it is well-known that some nations prepare an intoxicating liquor from milk by fermentation. There is reason to think that previous to fermentation, it is like cane sugar converted into grape sugar; and at all events milk does not ferment until an acid has been formed in it, which acid converts lactine into grape sugar.

Sugar of milk forms two compounds with oxide of lead: first, neutral, $C_{24} H_{19} O_{19}, 5\ PbO$: second basic, $C_{24} H_{19} O_{19}, 10\ PbO$.

Mucic Acid, $C_{12} H_8 O_{14} + 2\ HO$, is formed when diluted nitric acid acts on sugar of milk, gum, or mannite. It is a white crystalline powder, of a feebly acid taste, soluble in 6 parts of boiling water, which deposits nearly the whole on cooling. Its solution when long heated and evaporated, yields the *modified mucic acid.* Mucic acid dissolves in oil of vitriol with a crimson colour. When heated it blackens, and yields among other products, *pyromucic acid.*

Mucic acid is bibasic, and forms two series of salts, one with 2 eq. fixed base, the other with 1 eq. fixed base, and 1 eq. water.

These salts have little interest. The *mucate of oxide of ethyle* or *mucic ether*, crystallizes in 4-sided prisms, soluble in hot water. When boiled with a base, it yields alcohol, and mucate of the base. Its formula is $C_{12} H_8 O_{14} + 2\, Ae\, O$.

Modified mucic acid is more soluble in water, soluble in alcohol, from which solution it is deposited in square tables. Its aqueous solution, saturated at the boiling point, deposits on cooling ordinary mucic acid. Its salts are more soluble than the mucates, but the acid in them easily passes into the ordinary acid. It is probable that the modified acid contains 1 eq. of water more than the other.

Pyromucic acid, $C_{10} H_3 O_5 + H\, O$, is formed by the dry distillation of mucic acid. 1 eq. of mucic acid, $C_{12} H_{10} O_{16}$, contains the elements of 1 eq. pyromucic acid, $C_{10} H_4 O_6$, 6 eq. water, $H_6 O_6$; and 2 eq. carbonic acid, $C_2 O_4$. Pyromucic acid forms brilliant white scales, fusible at 266°, and volatilizes completely at a temperature somewhat higher. It is soluble in water and alcohol. Its salts are not important. *Pyromucate of oxide of ethyle*, $C_{10} H_3 O_5$, Ae O, is a solid crytallisable compound, fusible at 93° volatile at 410°, Chlorine acts on this ether, forming a new compound, $C_{14} H_8 Cl_4 O_6$, the constitution of which is quite uncertain.

4. *Sugar of mushrooms*. Wiggers obtained from ergot of rye a saccharine compound, crystallising in transparent rhombic prisms, soluble in water and alcohol, and susceptible of the vinous fermentation. An analysis of this sugar gave the formula $C_{12} H_{13} O_{13}$, that is, grape sugar, *minus* 1 eq. water. This may be a distinct kind of sugar; but the mushroom sugar of Braconnot is *mannite* or manna sugar.

We have seen that starch and woody fibre may be converted into grape sugar by boiling with dilute sulphuric acid: in like manner, salicine and phloridzine, boiled with the same acid, yield saliretine and phloretine, in each case along with grape sugar. But the action of the infusion of malt, is still more singular; we have seen that starch by contact with infusion of malt is rapidly converted into grape sugar. This action is ascribed to the presence of *diastase*, a nitrogenised body which exists in malt, and which, while it causes the conversion of starch into sugar, itself disappears. The action is not fully understood, but there is no doubt that when seeds germinate, the starch they contain is in this manner rendered soluble, and conveyed, as sugar, to all parts of the plant, there to be converted into woody fibre by a process the inverse of that by which woody fibre is converted into sugar. This latter is seen in the ripening of fleshy fruits, where a quantity of cellular matter (lignine) disappears, and the proportion of sugar very much increases.

VINOUS OR ALCOHOLIC FERMENTATION.

This name is given to that change by which sugar is resolved into alcohol and carbonic acid, by contact with a ferment. The sugar must be dissolved in water, and the solution must be exposed to a temperature of from 40° to 86°. If a ferment, such as yeast, be added, the sugar soon disappears, carbonic acid is given off in large quantity, and the liquid is found to contain alcohol, which may be separated by distillation. Now, grape sugar, $C_{12} H_{14} O_{14}$, contains the elements of 2 eq. alcohol, 4 eq. carbonic acid, and 2 eq. water, $2 (C_4 H_6 O_2) + 4 C O_2 + 2 H O$; and, by very exact experiments it has been proved that 100 parts of grape sugar yield only 47·12 of alcohol, 44·84 of carbonic acid, together 91·96 parts, the loss, 9·04 parts being the 2 eq. of water separated. On the other hand, cane sugar, $C_{12} H_{11} O_{11}$, requires the addition of 1 eq. of water to yield 2 eq. alcohol, and 4 eq. carbonic acid, $= 2 (C_4 H_6 O_2) + 4 C O_2$; and here also experiment has demonstrated, that 100 parts of cane sugar yield 53·727 parts of alcohol and 51·298 of carbonic acid, together 105·025; the increase, or 5·025 parts being due to the 1 eq. of water taken up to form dry grape sugar, $C_{12} H_{12} O_{12}$, into which cane sugar is converted before it undergoes fermentation. These facts prove that the ferment takes no direct part in the reaction, but only acts by inducing a state of change.

A considerable number of substances, if in a state of decomposition, act as ferments on a solution of sugar : among these are, besides yeast, vegetable gluten, albumen, caseine or fibrine, and the corresponding animal substances ; also animal matter generally, if in a state of putrefaction.

The only explanation we can give is that the particles of these bodies, being in a state of decomposition, are in motion, and by communicating, mechanically, an impulse or motion to the particles of the sugar, destroy the balance of affinities to which the existence of sugar is owing ; and thus give rise to a new balance or equilibrium, more stable under the given circumstances. The elementary particles of the sugar being disturbed in their previous arrangement, group themselves according to their individual affinities, and while the carbon forms, on one side, a compound containing all the hydrogen (alcohol), it yields on the other, a compound containing the greater part of the oxygen (carbonic acid).

When a natural juice, as that of the grape, ferments, some of the various substances it contains undergo a decomposition, probably of an analogous kind, giving rise to other new products, which are important in regard to the flavour of the liquid (wine, beer, or spirits), produced in the fermentation. Thus all wine contains œnanthic ether; potato spirit contains the oil of potato spirit (*fusel oel.* German): grain spirit contains a similar oil. It is not improbable, that besides the vinous fermentation which takes place in the greater part of the sugar, a peculiar reaction occurs, between a portion of the sugar and the ferment (or some other nitrogenised compound present), the result of which is the production of these peculiar oily liquids. The *bouquet*, or so much prized flavour of the finer wines, is doubtless owing to some etherial compound produced in a similar way, but the origin, properties, and composition of which are as yet altogether unknown. It may be mentioned here, however, that œnanthic ether, which is the cause of that peculiar smell which belongs to all wine, and is so marked that we can at once tell, after many weeks or months, that an empty bottle has formerly contained wine, is a compound of oxide of ethyle with a fatty acid; and the oil of potato spirit is a compound analogous to alcohol; the hydrated oxide of a radical *amyle*, $C_{10}H_{11}$.

VISCOUS FERMENTATION.

When certain saccharine juices, such as those of beet-root, carrots, onions, &c. are exposed to a temperature of from 86° to 104°, a peculiar fermentation takes place. The sugar disappears, but instead of alcohol and carbonic acid, there are obtained *mannite, lactic acid*, and a mucilaginous substance, having the composition of gum; this latter renders the liquid ropy, and viscid, hence the name given to the process.

The composition of mannite is . . . $C_6\ H_7\ O_6$
That of lactic acid is . . . . . $C_6\ H_5\ O_5$

Together . . . . . . $C_{12}\ H_{12}\ O_{11}$

It is evident, therefore, that 1 eq. of dry grape sugar, $C_{12}\ H_{12}\ O_{12}$, losing 1 eq. oxygen, might give rise to mannite and lactic acid. The gum has the same composition as sugar, so that we are led to believe that the nitrogenised constituents of the juice are acted on by the sugar, from which they obtain oxygen; and that these compounds are themselves decomposed by the oxygen, mannite, and lactic acid, which are very permanent, being produced from the sugar.

This peculiar fermentation is produced when cheese is added to a solution of sugar, and the whole kept at a proper temperature.

Mannite, $C_6\ H_7\ O_6$ occurs as the chief ingredient of manna. It is also found in certain juices, in mushrooms, in roots, such as that of celery, and is formed artificially as above described. It is easily purified by solution in alcohol and crystallisation. It forms, when crystallised in water, large prisms, of a weak sweet taste. It is not susceptible of the vinous fermentation. Nitric acid and permaganate of potash act on it as on sugar. Concentrated arsenic acid gives it a brick red colour.

Lactic Acid, $C_6 H_5 O_5 + H O$, so called because it occurs in sour milk, is also formed abundantly, as above described, in a peculiar fermentation of certian saccharine juices at a high temperature. In milk it is derived from the sugar of milk ; and by neutralising sour milk with carbonate of soda, adding sugar of milk, allowing it again to become acid, again neutralising, and so on in succession, as long as the caseine causes the peculiar change to take place, it may be obtained in large quantity. A still easier process is to dissolve 14 parts of cane sugar in 60 of water, and to add 4 of moist cheese and a sufficient quantity of prepared chalk. The mixture being kept some time at from 77° to 86° F. will at last become quite thick with crystals of lactate of lime. If the action of the caseous ferment be pushed further, and at a higher temperature, the lactate of lime is not obtained, but in its place *butyrate of lime* in large quantity. See *Butyric acid.* The above quantities will yield about 13 parts of lactate after it has been purified by crystallisation ; besides from 1½ to 2 parts of mannite. The acid of sour crout is lactic acid, and by boiling the juice of sour crout with chalk or carbonate of zinc, lactate of zinc or of lime may be obtained.

From the lactate of lime, lactic acid may be obtained by the action of oxalic acid, which removes the lime as oxalate. The filtered solution is lactic acid, which is concentrated by evaporation, and purified by solution in ether. From the lactate of soda, lactate of zinc may be obtained by adding chloride of zinc to the hot saturated solution ; on cooling, lactate of zinc, being sparingly soluble in cold water, crystallises. This salt, acted on by barytic water, yields lactate of baryta, from which sulphuric acid removes the baryta, and the filtered liquid is pure diluted lactic acid.

In its most concentrated form, hydrated lactic acid is a syrupy liquid of a very strong but pleasant acid taste. Its Sp. G. is 1·215. Its formula $C_6 H_5 O_5 + HO = C_6 H_6 O_6$. It is therefore polymeric with dry grape sugar and with gum ; both of which are $C_{12} H_{12} O_{12}$. At 482° the hydrate is decomposed, and yields a solid crystalline sublimate, $C_6 H_4 O_4$, which has been called anhydrous lactic acid, or sublimed lactic acid. This compound dissolves readily in hot water, and the solution if evaporated yields the original hydrate $C_6 H_6 O_6 = C_6 H_4 O_4 +$

$2 HO$. But when the acid is neutralised by bases, only one of the 2 eq. of water taken up by the sublimed acid is replaced by a base; and consequently we cannot look on the sublimed acid as the true anhydrous acid. The anhydrous acid, as it exists in the lactates, is $C_6 H_5 O_5$; and the sublimed acid is not lactic acid, but is converted into lactic acid when boiled with water.

The general formula for the lactates is $C_6 H_5 O_5, MO$. The lactates of the alkalies are very soluble and deliquescent: that of lime is less soluble in cold water and crystallises readily. The lactate of zinc is sparingly soluble in cold water, and is hence well adapted for the extraction and purification of the acid.

XIX. METHYLE. $C_2 H_3 = Mt$.

This is the hypothetical radical of a numerous series of compounds, entirely analogous to those of ethyle. There is the *oxide of methyle*, $Mt O$, analogous to oxide of ethyle; and the *hydrated oxide of methyle* $Mt O, HO$, analogous to alcohol. This last is the compound from which all the others are obtained. The extraordinary analogy between ethyle and methyle will enable us to describe the compounds of the latter very briefly.

1. Hydrated Oxide of Methyle. $Mt O, HO$.

SYN. *Pyroxilic Spirit.* This compound is one of the chief products of the destructive distillation of wood, and is found in the watery portion, along with acetic acid, acetone, acetate of oxide of methyle, and several other etherial liquids, besides portions of the oily matter of the tar dissolved in them.

By rectification with chloride of calcium, the pyroxilic spirit, which combines with that salt, is separated from several other liquids which distil over in the heat of the vapour bath. The residue, if mixed with its own bulk of water, and again heated in the vapour bath, now gives off the pyroxilic spirit, which is still mixed with water. It is purified by rectification with quicklime, which also destroys any acetate of methyle that may be present.

Pure hydrated oxide of methyle is a liquid very similar to alcohol, having the same density, and the same degree of inflammability. Its odour is peculiar and etherial. It boils at about 140° or 150°.

When heated with peroxide of manganese, water, and sulphuric acid, it yields various products, among which the chief are, *formic acid* and *formomethylal*. It is decomposed by nitric acid, yielding oxalic acid, and by chlorine, yielding new products. It dissolves resins, and is used in making varnishes. It forms with baryta a crystalline compound $BaO + MtO, HO$; and, with chloride of calcium, another crystalline body in large hexagonal tables, $CaCl + 2(MtO, HO)$.

By the action of platinum powder, pyroxilic spirit is oxidised into formic acid, which bears the same relation to it that acetic acid does to alcohol.

2. Oxide of Methyle. $MtO = (C_2 H_3) O$.

This compound is obtained, like ether (oxide of ethyle) when the preceding compound is distilled with its own volume of oil of vitriol; it escapes as an inflammable gas. Like oxide of ethyle, it is a base and neutralises acids. It even forms a neutral sulphate, which oxide of ethyle cannot do. It is worthy of notice, that oxide of methyle is polymeric with alcohol; for $C_4 H_6 O_2 = 2 (C_2 H_3 O)$: so that these two bodies have the same composition, in 100 parts; that is, the same relative proportions of the same elements, but a very different absolute amount: the equivalent of alcohol being twice as heavy as that of oxide of methyle. The constitution of these compounds, moreover, is different, for one is a hydrate, $C_4 H_5 O + HO$; while the ether is an anhydrous oxide, $C_2 H_3 O$.

3. *Chloride of methyle*, $C_2 H_3, Cl = MtCl$, is a gas, of an etherial smell, inflammable, of Sp. G. 1·1737. It is formed by the action of sulphuric acid and chloride of sodium on pyroxilic spirit. By the action of chlorine, aided by the sun's rays, it yields several new compounds containing chlorine.

4. *Iodide of methyle*, $C_2 H_3, I = Mt I$, is obtained by distilling 12 parts of pyroxilic spirit, 8 of iodine, and 1 of phosphorus. It is a liquid, boiling between 102° and 122°. The *fluoride* and *cyanide* of methyle are analogous liquids.

5. *Sulphuret of methyle*, $C_2 H_3, S = Mt S$, is best formed by the action of a current of chloride of methyle on sulphuret of potassium dissolved in alcohol. $MtCl + KS = MtS + KCl$. It is a mobile liquid, of a very offensive alliaceous odour, boiling at 104°. Its Sp. G. in the liquid form is 0·845; in the form of vapour, it is 2·115. With chlorine, it gives rise to several new compounds. The *hydrosulphuret* of *sulphuret of methyle* (corresponding to mercaptan) I obtained by distilling the double sulphate of methyle and potash with the hydrosulphuret of sulphuret of potassium. $(KO, MtO, 2SO_3) + HS, KS = 2(KO, SO_3) + HS, MtS$. Its formula is $HS, MtS = C_2 H_3, S + HS$. It is a colourless liquid, lighter than water, which boils at 70°, and acts on the oxides of mercury and lead exactly as mercaptan does. Its odour is most offensive, resembling that of leeks highly concentrated.

SALTS OF OXIDE OF METHYLE.

1. *Neutral Sulphate.* Mt O, SO_3, is obtained when pyroxilic spirit is distilled with a large excess of sulphuric acid. It forms an oily liquid, of a slightly alliaceous smell. It boils at 370°. Boiling water decomposes it into acid sulphate and hydrate of oxide of methyle. When heated with chlorides, cyanides, &c., it yields the compound of methyle with chlorine, cyanogen, &c.; with a salt of benzoic, succinic, or other organic acid, it yields benzoate, &c. of oxide of methyle. Ammonia converts it into *sulphamethylane.*

2. *Bisulphate of Oxide of Methyle.* SYN. *Sulphomethylic Acid.* HO, Mt O, $2SO_3$, is perfectly analogous to sulphovinic acid, and forms double salts, such as that of potash, KO, Mt O, $2SO_3$, which are often called sulphomethylates, and correspond exactly to the sulphovinates. The acid sulphate itself may be obtained in crystals, which are very soluble and very acid. It is best obtained by the action of hot water on the neutral sulphates. The double salts, or sulphomethylates, are of no particular importance. They crystallise readily.

3. *Nitrate of Oxide of Methyle,* Mt O, NO_5, is obtained when pyroxilic spirit is distilled with nitrate of potash and sulphuric acid. It is an oily liquid, the vapour of which if heated beyond 248° explodes violently.

The neutral carbonate of methyle is not known; but double carbonates, analogous to those of ethyle with alkalies, may be prepared in the same way as those compounds.

4. *Oxalate of Oxide of Methyle,* Mt O, $C_2O_3 = C_4H_3O_4$, is obtained in a manner analogous to that in which oxalic ether is prepared. It forms a crystalline solid, soluble in alcohol and pyroxilic spirit, which deposit it in large crystals. By the action of dry ammonia, it is converted into *oxamethylane* (analogous to oxamethane), which is the *oxamate of oxide of methyle,* $C_6H_5NO_6 = C_2H_3, O + C_4H_2NO_5$. Liquid ammonia converts it into oxamide, as is the case with oxalic ether, only here pyroxilic spirit and not alcohol is formed at the same time. $C_2H_3O, C_2O_3 + NH_3 = C_2H_3O, HO + C_2O_2, NH_2$. This is perhaps the easiest way of obtaining oxamide in large quantity.

Bisulphuret of carbon and hydrated cyanic acid act on pyroxilic spirit exactly as on alcohol, producing analogous compounds.

5. *Benzoate of Oxide of Methyle,* Mt O, Bz O, is best obtained by distilling dry benzoate of lime or soda with neutral sulphate of methule. It is an oily liquid, of a balsamic odour, analogous in other respects to benzoic ether.

6. *Acetate of Oxide of Methyle*, $Mt\,O, Ac\,O_3$, is obtained in the same way as acetic ether, which it resembles. It occurs in considerable quantity in raw pyroxilic spirit, and even in that which has only been purified by rectification. When quicklime is used in the rectification, it is destroyed, yielding an additional quantity of the pure hydrate of oxide of methyle. It is very volatile and inflammable, and for most purposes its presence in the wood spirit is not at all injurious. It is isomeric with formiate of oxide of ethyle: for $C_2\,H_3\,O + C_4\,H_3\,O_3 = C_4\,H_5\,O + C_2\,HO_3$.

The mucate of oxide of methyle is a crystalline solid, analogous in its preparation and properties to the corresponding salt of ethyle.

The action of chlorocarbonic acid on pyroxilic spirit is exactly analogous to its action on alcohol, producing an oily liquid, $C_4\,H_3\,Cl.\,O_4 = C_2\left\{\begin{matrix}O_3\\ Cl.\end{matrix}\right. + C_2\,H_3\,O$. By the action of ammonia, this liquid produces a compound, *urethylane*, (corresponding to *urethane*) $C_4\,H_5\,NO_4$ or $C_8\,H_{10}\,N_2\,O_8 = C_2\,H_4\,N_2\,O_2 + 2\,(C_2\,H_3\,O, CO_2)$; that is, a compound, possibly, of 1 eq. urea, with 2 eq. neutral carbonate of methyle.

When a current of ammonia is made to act on the neutral sulphate of methyle, there is produced a crystalline compound, $C_2\,H_5\,NS_2\,O_6$, which has been called *sulphamethylane*, and may be viewed as oxamethylane, in which sulphamide, SO_2, NH_2, has been substituted for oxamide, $C_2\,O_2$, NH_2; or SO_2 for $C_2\,O_2$. It may also be considered, if oxamethylane be the oxamate of oxide of methyle, $C_2\,H_3\,O + C_4\,H_2\,NO_5$, as composed of oxide of methyle and a peculiar acid, formed of hyposuphuric acid and amide; $C_2\,H_3\,O + (S_2\,O_5, NH_2)$.

When hydrated oxide of methyle is oxidised by means of platinum powder, it is finally converted into pure formic acid. There is evidently, therefore, the same relation between methyle and formic acid, as between ethyle and acetic acid; and on comparing the formulæ of pyroxilic spirit and of formic acid, $C_2\,H_3\,O, HO$ and $C_2\,HO_3, HO$, we perceive that the former, to be converted into the latter, must have lost 2 eq. of hydrogen, and taken up 2 eq. of oxygen. This is exactly what takes place with alcohol, and there can be no doubt, that the pyroxilic spirit yields an intermediate compound, exactly analogous to aldehyde, although this has not yet been isolated. Such a compound would be the hydrated protoxide of a derived radical, *formyle*, analogous to acetyle, of which formic acid is the hydrated peroxide; and its formula would be $(C_2\,H)\,O + HO$. We shall, therefore, assume the existence of this radical, and proceed to describe its compounds, which are quite analogous to those of acetyle.

XX. FORMYLE. $C_2H = Fo$.

This radical is unknown in a separate form, as are its protoxide and deutoxide, corresponding to aldehyde and aldehydic acid. But when hydrated oxide of methyle is distilled with sulphuric acid, water, and peroxide of manganese, a volatile liquid is obtained, which is a mixture of formiate of oxide of methyle and another liquid called methylal. When purified, this latter has the formula $C_6H_8O_4$, which indicates, that it is composed of C_2HO, HO, or hydrated oxide of formyle, and 2 eq. of oxide of methyle, $2(C_2H_3O)$. This compound, briefly, $FoO, HO + 2 MtO$, corresponds to acetal in the series of ethyle; acetal being $AcO, HO + AeO$.

Formic Acid. $C_2HO_3, HO = FoO_3, HO$.

This remarkable acid occurs in the red ant, *formica rufa*, and may be obtained, in a diluted and impure state, by infusing these insects in water. Its production from pyroxylic spirit has been described above. It may also be prepared by distilling a mixture of starch or sugar with peroxide of manganese, water, and sulphuric acid; and it is formed under a great variety of circumstances from many organic compounds.

To prepare the hydrated acid pure and concentrated, the dry formiate of lead, PbO, FoO_3, is decomposed by sulphuretted hydrogen gas, and the vapour of the formic acid condensed in a well-cooled receiver. It is boiled for a few moments to expel any sulphuretted hydrogen. It is a clear liquid of Sp. G. 1.235, fuming slightly, and has a very pungent acid smell. Below 32° it crystallises in brilliant scales. It boils at 212°, and its vapour is inflammable, burning with a blue flame. This is probably owing to the formation of carbonic oxide, for the acid C_2HO_3, HO, contains the elements of 2 eq. carbonic oxide, C_2O_2, and 2 eq. water, H_2O_2.

With 1 eq. of water it forms the second hydrate $FoO_3 + 2HO$, which much resembles the first in properties. Its boiling point is 221°, and its Sp. G. is 1.110.

Both these hydrates are highly corrosive; a drop of either on any delicate portion of the skin causes a severe burn, which blisters, suppurates, and is very painful and difficult to heal. In this respect, the formic acid can only be compared to hydrofluoric and hydrated cyanic acids.

A weaker acid is obtained by distilling formiate of soda, lime, or lead, with sulphuric acid, previously diluted with half its weight of water. Ten parts of formiate of lime, 8 of oil of vitriol, and 4 of water, yield 9 of formic acid, of Sp. G. 1.075.

The salts of the acid are best prepared from the weak and impure acid obtained by distilling a mixture of 10 parts of starch, 37 of peroxide of manganese, 30 of oil of vitriol and 30 of water. These materials yield 3.35 parts of formic acid, such that 100 parts neutralise 15 of dry carbonate of soda. From this acid, the formiate of lead may be easily prepared and purified; and from it, by the addition of carbonate of soda, formiate of soda may be obtained.

Formic acid is easily recognised by the action of sulphuric acid, which decomposes, without blackening, both it and its salts, causing the disengagement of pure carbonic oxide. It also reduces the oxides of all the noble metals, and is itself oxidised into carbonic acid. Formic acid not only reduces the oxides, but also, in most cases, the soluble salts, of the noble metals. 1 eq. formic acid can reduce 2 eq. of a protoxide, such as that of silver, $2\,AgO + C_2HO_3 = Ag_2 + HO + 2CO_2$; or 1 eq. of a deutoxide, such as that of mercury; $HgO_2 + C_2HO_3 = Hg + HO + 2CO_2$.

Formic acid is a very powerful acid, and forms salts with bases, all of which are soluble. They are generally similar to the acetates; but yet quite distinct. Many metallic formiates, when heated in close vessels, give off carbonic acid and carbonic oxide, leaving the metal reduced: others give off carbonic oxide, leaving the oxide.

Formiate of ammonia, NH_4O, C_2HO_3, contains the elements of hydrocyanic acid and water, $C_2NH + 4HO$; and is converted into these compounds when its vapour is passed through a red-hot tube. *Formiate of oxide of ethyle*, prepared like the acetate, is a volatile ethereal liquid, with a peculiar aromatic smell. The corresponding salt of oxide of methyle is quite analogous. *Formiate of potash* is very deliquescent. *Formiate of soda* is also very soluble, but may be obtained in crystals. It is a very powerful reducing agent, both in the moist and dry way. In the former, it reduces the noble metals, in the latter, at a red heat, by virtue of the carbonic oxide it gives off, it reduces most of the reducible metals, such as lead, copper, antimony, arsenic, cobalt, nickel, &c. *Formiate of lead* is sparingly soluble in cold water, and is therefore easily purified, and serves to prepare formic acid and formiate of soda. *Formiate of deutoxide of mercury* and *formiate of protoxide of mercury* both exist. When red oxide of mercury is dissolved in cold formic acid, the former salt is produced; but the slightest heat causes an effervescence, while formiate of the protoxide is deposited in silvery scales like the acetate. These, when warmed, are decomposed with effervescence and deposition of metallic mercury. *Formiate of silver* resembles the acetate; but is very easily decomposed by heat, the metal being reduced.

COMPOUNDS OF FORMYLE WITH CHLORINE, ETC.

When chlorine or hypochlorites act on oxide of methyle, hydrated oxide of methyle, and chloride of methyle, a great variety of new compounds are produced, corresponding in most cases to the compounds obtained by the action of chlorine, &c., on alcohol, ether, and chloride of ethyle. Our space forbids us to give the details of these decompositions; but we may mention that two of the compounds formed by the action of chlorine on the compounds of ethyle and acetyle, may be viewed as *protochloride* and *bichloride of formyle.* These are $C_4H_2Cl_2 = 2\,(C_2\,H, Cl)$; and $C_4H_2Cl_4 = 2\,(C_2\,H, Cl_2)$. The *perchloride of formyle*, $FoCl_3 = C_2H, Cl_3$, is also produced from a compound of the ethyle series, namely from chloral, by the action of alkalies. It is an oily liquid of a sweet taste and ethereal smell. When acted on by alkalies, it yields chlorides and formiates; thus, with potash, $C_2HCl_3 + 4\,KO = 3\,KCl + KO, C_2HO_3$.

When acted on by chlorine, perchloride of formyle yields perchloride of carbon $C_2Cl_4 = C_2Cl, Cl_3$, just as perchloride of acetyle, C_4H_3, Cl_3 yields sesquichloride of carbon $C_4Cl_6 = C_4Cl_3, Cl_3$.

Perbromide of formyle is obtained from bromal. Periodide of formyle, obtained by the action of alcohol on iodine and potash, is a yellow crystalline, volatile, solid, having an odour analogous to that of saffron.

When chlorine acts on oxide of methyle, C_2H_3O, it produces, by substitution of chlorine for hydrogen, the compounds $C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right.O$; $C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right.O$; and finally, C_2Cl_3, O. The second may be considered as formic acid, $C_2\,H\,O_3$, in which two-thirds of the oxygen are replaced by chlorine, $C_2\,H\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$. It will then be an oxychloride of formyle, analogous to oxychloride of acetyle.

When chlorine acts on chloride of methyle, $C_2\,H_3\,Cl$, three compounds are formed by substitution. These are, 1st, $C_2\,H_2\,Cl_2 = C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right., Cl$; 2nd, perchloride of formyle, $C_2\,HCl_3 = C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right., Cl$; and 3rd, as before explained, perchloride of carbon, $C_2\,Cl_4 = C_2\,Cl_3, Cl$.

The action of chlorine on sulphuret of methyle, $C_2\,H_3, S$, appears to yield, $C_2\left\{\begin{matrix}H_2\\Cl\end{matrix}\right.S$; $C_2\left\{\begin{matrix}H\\Cl_2\end{matrix}\right.S$; and $C_2\,Cl_3\,S$.

The action of chlorine on oxalate, benzoate, and acetate of oxide of methyle is quite analogous to its action on the corresponding compounds of ethyle, producing the oxalate, benzoate, and acetate of oxychloride of formyle, $C_2\ O_3 + C_2\ H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$; $C_{14}\ H_5\ O_3, + C_2\ H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$; and $C_4\ H_3\ O_3 + C_2\ H \left\{\begin{matrix}O\\ Cl_2\end{matrix}\right.$. These curious results, like those which precede them, are here merely indicated, as we have explained the principle of their formation under the heads of ethyle and acetyle.

In some specimens of raw pyroxilic spirit there occurs a large proportion of a peculiar volatile liquid, which has been called *lignone* or *xylite*. As its constitution is quite uncertain, although it is believed to contain some compound of oxide of methyle, we shall state what is known of it when treating of the products of the dry distillation of wood.

XXI. CETYLE. $C_{32}\ H_{33} = Ct$.

This is the hypothetical radical of a series of compounds, derived from spermaceti. The principal one is *ethal*, the hydrated oxide of cetyle, analogous to alcohol.

Hydrated Oxide of Cetyle. $C_{32}\ H_{33}\ O, H\ O = Ct\ O, H\ O$.

Syn. *Ethal.* This compound exists in spermaceti, in combination with margaric and oleic acids. When spermaceti is digested with strong caustic potash, a soap is produced; and this being decomposed by sulphuric acid, yields a fatty mixture, composed of margaric and oleic acids and ethal. The whole is acted on by baryta, with which the acids unite; and the ethal is dissolved from the mixture by cold alcohol. It is afterwards purified by means of ether.

Ethal forms a white crystalline solid, like wax, fusible about 118°, volatile at a higher temperature, soluble in alcohol. As above mentioned, it is analogous to alcohol; and although the oxide of cetyle has not yet been obtained in a separate form, yet there have been formed the *chloride of cetyle*, and the *double sulphate of oxide of cetyle and potash*, analogous to the corresponding compounds of ethyle.

When ethal is repeatedly distilled with anhydrous phosphoric acid, it loses the elements of 2 eq. of water, yielding a new compound, cetene$=C_{32}\ H_{32}$, analogous to olefiant gas or etherine. It is an oily inflammable liquid.

XXII. AMYLE. $C_{10}\ H_{11} = Ayl$.

This is the hypothetical radical of a series of compounds, derived from oil of potato spirit, which is itself, when pure, the hydrated oxide of amyle, analogous to alcohol. Both the radical and its anhydrous oxide are unknown in the separate state; but a sufficient number of compounds has been obtained to render its existence highly probable.

Hydrated Oxide of Amyle. $C_{10}H_{11}O, HO = Ayl\,O, HO$.

Syn. *Oil of potato spirit;* in German, *Fuseloel.* This compound distils over towards the end of the first distillation of spirits made from potatoes, rendering these last portions of the spirit milky and very offensive. It separates on standing as an oily liquid, which is washed with water to remove alcohol, dried by chloride of calcium, and rectified till its boiling point becomes steady at 269° or 270°. It is then pure.

It is a colourless oily liquid, very mobile, of a strong and nauseous odour, which produces stupefying effects. Its vapour, when inhaled, causes cough and spasmodic dyspnœa, resembling asthma, often followed by vomiting. Its taste is very acrid and nauseous. Its Sp. G. is 0·812. At —4° it crystallises in shining scales. When heated with dry hydrate of potash it is oxidised, hydrogen being given off, and the potash is found combined with valerianic acid, $C_{10}H_9O_3$. When distilled with anhydrous phosphoric acid, it yields a new carbohydrogen, *amilene*, $= C_{10}H_{10}$.

The *chloride of amyle* has not yet been obtained; but the *bromide* and *iodide* are formed when the hydrated oxide is distilled along with phosphorus and bromine or iodine. They are both heavy oily liquids, and their formulæ are Ayl Br. and Ayl I.

The *bisulphate of oxide of amyle* or *sulphamilic acid*, $Ayl\,O, HO, 2SO_3$, is analogous to sulphovinic acid. With bases, it forms double salts, the formula of which is $MO, Ayl\,O, 2SO_3$, which are soluble in water and crystallisable. The solutions, when boiled, yield hydrated oxide of amyle, free sulphuric acid, and a neutral sulphate.

The *acetate of oxide of amyle* is an etherial liquid, analogous to acetic ether. Its formula is $C_{14}H_{14}O_4 = C_{10}H_{11}O, C_4H_3O_3 = Ayl\,O, Ac\,O_3$.

The *hydrosulphuret of sulphuret of amyle*, $Ayl\,S, HS$, is prepared in the same way as mercaptan, to which it is quite analogous. It is an oily liquid, boiling at 243°, of Sp. G. 0·835. It has, like the corresponding compounds of ethyle and methyle, a most penetrating odour of onions; and, like them, it acts on red oxide of mercury, forming a white crystalline compound $Ayl\,S, HgS$.

The *sulphocarbonate of oxide of amyle*, very analogous to the bisulphocarbonate of oxide of ethyle, is formed when bisulphuret of carbon acts on a solution of potash in oil of potato spirit.

OXIDATION OF HYDRATED OXIDE OF AMYLE.

Valerianic Acid. $C_{10}H_9O_3, HO$.

It has already been mentioned, that when oil of potato spirit is heated with dry hydrate of potash, hydrogen is given off, and valerianate of potash is formed. Here the oil, $C_{10}H_{11}O, HO$, loses 2 eq. hydrogen, and gains 2 eq. oxygen; so that valerianic acid stands to amyle in the same relation as acetic acid to ethyle, and formic acid to methyle. The acid is easily separated by distilling the salt of potash with diluted sulphuric acid. In composition and in all its properties, it agrees with the native valerianic acid, obtained by distilling the root of *valeriana officinalis* with water.

Valerianic acid is a limpid, oily fluid, of a disagreeable and peculiar smell. Its Sp. G. is 0·944, and it boils at 270°. With bases, it forms soluble salts, which have a sweet taste.

The action of chlorine on hydrated oxide of amyle gives rise to the formation of a compound, *chloramilal,* supposed to be analogous to chloral, but the composition and nature of which are not fully known.

Amilene, the carbo-hydrogen obtained by distilling hydrated oxide of amyle with dry phosphoric acid, has the formula $C_{10}H_{10}$, and is, like cetene, isomeric with olefiant gas.

XXIII. GLYCERYLE. $C_6H_7 = Gl$.

This is the hypothetical radical of glycerine, a basic compound which exists in all neutral fat oils combined with oily acids.

Hydrated Oxide of Glyceryle. $C_6H_7O_5 + HO = Gl\,O_5\,H\dot{O}$.

Syn. *Glycerine.* To obtain it, olive oil is converted into plaster by long boiling with litharge and water. When the plaster is completely formed, the glycerine is found dissolved in the water. It is purified from lead by sulphuretted hydrogen, and is then concentrated in the vapour bath and finally in vacuo. When pure, it forms a viscid syrup, colourless or slightly yellow. It has a decided sweet taste, and its Sp. G. is 1·252. By the action of heat it is decomposed, yielding a peculiar volatile compound, *acroleine,* which attacks the eyes most powerfully. This substance has lately been studied by Redtenbacher: we shall give his results when treating of the action of heat on fat oils.

With sulphuric acid, glycerine forms an acid sulphate C_6H_7

$O_5, HO, 2SO_3$; which forms double salts, analogous to the sulphovinates, the formula of which is, $MO, GlO_5, 2SO_3$.

Having now briefly described the known or admitted organic radicals and their derivatives, we proceed to consider the organic acids whose composition is known, although we cannot speak with certainty of their constitution, their radicals being yet unknown.

ORGANIC ACIDS.

1. Citric Acid. $C_{12}H_5O_{11}, 3HO = \overline{Ci}, 3HO$.

This acid is found in many vegetable juices, especially those of sour fruits, as the lemon, lime, orange, red currant, &c. It is extracted by adding chalk to the acid juice, by which means an insoluble citrate of lime is formed. This is decomposed by diluted sulphuric acid with the aid of heat, and the solution, filtered from the sulphate of lime, gives on evaporation and cooling crystals of citric acid, consisting of $\overline{Ci}, 3HO + aq$. A slight excess of sulphuric acid promotes the crystallisation.

It forms large transparent crystals, very soluble in water, of a very strong and agreeable acid taste. A diluted solution is soon decomposed, becoming mouldy. By spontaneous evaporation of a saturated solution, crystals may be obtained, which are $\overline{Ci}, 3HO + 2aq$. At 212°, these lose the 2eq. of water of crystallisation. The other crystals, above mentioned, do not lose water at 212°, but melt at 256°; and when heated beyond 300°, both kinds are decomposed. Heated with oil of vitriol in excess, citric acid is decomposed, yielding,

From 1 eq. citric acid	$C_{12}H_8O_{14}$
2 eq. carbonic acid	$C_2\ \ O_4$
2 eq. carbonic oxide	$C_2\ \ O_2$
2 eq. acetic acid	$C_8H_6O_6$
2 eq. water	H_2O_2
	$C_{12}H_8O_{14}$

In like manner, when fused with caustic potash, citric acid is resolved into 2 eq. of acetic acid, 2 eq. oxalic acid, and 2 eq. water.

When citric acid is added to lime-water, the liquid remains clear, but when heated becomes turbid, and deposits citrate of lime. This character serves to distinguish citric acid from most other vegetable acids.

SALTS OF CITRIC ACID.

Citric acid is tribasic, and forms three series of neutral salts, that is, of salts with 3 eq. of base, whether fixed base or basic water. It also forms basic salts, of the formula $\overline{Ci}, 3\,MO + MO$ or $\overline{Ci}, 3\,MO + MO +$ aq. These basic salts correspond in constitution to the two forms of crystallised acid.

When a dry citrate, with 3 eq. of fixed, base is decomposed by an alcoholic solution of hydrochloric acid, so that no more water is presented to the citric acid than the 3 eq. of basic water derived from the hydrogen of the hydrochloric acid and the oxygen of the base, there are formed, from 3 eq. dry citric acid, 2 eq. of the acid with 1 eq. of water of crystallisation, and 3 eq. of the hydrated aconitic acid. $3\,(C_{12}\,H_5\,O_{11}, 3\,HO) = 2\,(C_{12}\,H_5\,O_{11}, 3\,HO + \text{aq.}) + 3\,(C_4\,HO_3, HO)$. This is the same change which takes place in citric acid when heated to a certain point, water being given off.

Citrate of Oxide of Ethyle, $\overline{Ci}, 3\,Ae\,O$, is an oily liquid of Sp. G. 1·142. By alkalies it is converted into citrates and alcohol.

Citrate of Potash occurs in three forms. $\overline{Ci}, 3\,KO$; $\overline{Ci}, \left\{\begin{matrix}2\,KO\\ HO\end{matrix}\right.$ and $\overline{Ci}\left\{\begin{matrix}KO\\ 2\,HO\end{matrix}\right.$. All are very soluble and crystallise with difficulty.

Citrate of Soda also forms three salts. 1. $\overline{Ci}, 3\,Na\,O + 11$ aq. This salt forms large regular crystals. 2. $\overline{Ci}, 2\,Na\,O, HO$; formed by adding to a solution of the preceding salt half as much citric as it already contains. It forms, by evaporation, needles of a very pleasant subacid taste. 3. $\overline{Ci}, Na\,O, 2\,HO$. Formed by adding to a solution of No. 1, as much citric acid as it already contains. This salt does not crystallise in water, but forms a gummy mass. A saturated alcoholic solution, however, deposits crystalline grains. *Citrate of baryta* forms two varieties. 1. $\overline{Ci}, 3\,Ba\,O + 7$ aq. which falls when citrate of soda is added to chloride of barium. 2. $2\,\overline{Ci}\left\}\begin{matrix}5\,Ba\,O\\ H\,O\end{matrix}\right. + 7\,\text{aq.} = \overline{Ci}\left\{\begin{matrix}2\,Ba\,O\\ H\,O\end{matrix}\right. + \overline{Ci}, 3\,Ba\,O + 7\,\text{aq.}$ This is deposited on cooling, when a boiling solution of citrate of soda is added to a boiling solution of chloride of barium and free citric acid. *Citrate of lime* also yields two salts. 1, neutral, $\overline{Ci}, 3\,Ca\,O + 4$ aq. formed by mixing chloride of calcium and citrate of soda. It is insoluble. 2, basic : $\overline{\text{Ci}}, 3\,CaO + CaO + aq.$ formed when citric acid is heated with excess of lime-water. The citrate of lime formed from lemon, or currant-juice, by chalk, is an impure mixture of the basic and neutral salts. *Citrates of lead,* 1. $\overline{\text{Ci}}, 3\,PbO + aq.$ 2. $\overline{\text{Ci}}, 2\,PbO, HO + 2\,aq.$: 3, basic: $\overline{\text{Ci}}, 3\,PbO + 3\,PbO.$: 4, also basic. $\overline{\text{Ci}}, 3\,PbO + PbO + aq.$ These are all sparingly soluble or insoluble, and are decomposed by washing. *Citrate of copper* is basic, $\overline{\text{Ci}}, 3\,CuO + CuO.$ *Citrate of silver* is a brilliant white, insoluble powder, $\overline{\text{Ci}}, 3\,AgO + aq.$ It loses its water under 80°. *Citrate of antimony and potash* is a double salt, $\overline{\text{Ci}}, Sb_2O_3 + \overline{\text{Ci}}, 3\,KO + 5\,aq.$ It forms hard, brilliant, white prisms, which lose their water at 212°.

ACTION OF HEAT ON CITRIC ACID.

The first effect of heat on crystallised citric acid is to melt it, and the next, to expel the water of crystallisation. The acid, if now dissolved, crystallises unchanged. But if the heat be continued, there is given off gas and inflammable vapours, and the residue is no longer citric acid but hydrated aconitic acid.

	1 eq. crystallised citric acid	C_{12}	H_5	$+O_{11}$	$3HO+2$ aq.
Yields, first,—	5 eq. of water . . .				$3HO+2$ aq.
then—	1 eq. aconitic acid (hydrated)	C_4	H_2	O_4	
	4 eq. carbonic oxide .	C_4		O_4	
	1 eq. acetone . . .	C_3	H_3	O	
	1 eq. carbonic acid . .	C		O_2	
		C_{12}	H_5	O_{11}	$+3HO+2$ aq.

When the heat is increased, other products appear, particularly two new acids: but these are derived from aconitic acid. They are *itaconic* and *citraconic acids.*

Aconitic Acid. $C_4HO_3, HO = \overline{\text{At}}.$

SYN. *Equisetic Acid.*—This acid occurs native in *aconitum napellus* and in *equisetum fluviatile.* It is formed by the action of heat on citric acid, as above. To obtain it, citric acid is heated till it ceases to give off inflammable vapours, and the residue, dissolved in alcohol, is treated with hydrochloric acid gas, which causes the formation of aconitic ether. The addition of water causes this to separate, and by caustic potash it is converted into aconitate of potash. From this aconitate of lead is prepared, and this salt, decomposed by sulphuretted hydrogen, yields the acid.

It forms indistinct crystals; and although the acid thus prepared has the same composition as that from aconite, and that from equisetum, yet each of the three varieties has some peculiarities. They may not, therefore, be identical, especially as two acids derived from malic acid, the maleic and paramaleic, or fumaric acids, have the same composition. The aconitic acid from citric acid, when heated, yields itaconic and citraconic acids: it is doubtful, at present, whether the other two varieties do so.

Aconitic acid, according to the present state of our knowledge, is monobasic, and the general formula of its salts is $\bar{At}, MO$. The aconitates are not important.

When aconitic acid (from citric acid) is heated to from 356° to 392°, it boils and yields a mixture of two acids; itaconic acid, which condenses in crystals, and citraconic acid, which appears as an oily liquid. When the distillation is very rapid, itaconic acid predominates; when it is slow, there is more citraconic acid. These two acids have both the formula $C_5 H_2 O_3, HO$.

Itaconic acid is readily purified by solution in hot water, as it crystallises with great facility. It is soluble in water, alcohol, and ether. When heated it is resolved into water and anhydrous citraconic acid. It is a monobasic acid, and its formula is $C_5 H_2 O_3, HO = \bar{It}, HO$. The formula of its salts is $\bar{It}, MO$. It also forms acid salts, the formula of which is $2\,\bar{It}, MO, HO$. The itaconates are not of special interest.

Citraconic acid is formed when the preceding acid is distilled, and then appears, in the anhydrous state, as a limpid oily liquid. It distils unaltered at 410°, and volatilises slowly at much lower temperatures. It attracts moisture from the air, forming a crystalline hydrate, which, when heated, is again resolved into water and anhydrous acid. The formula of the anhydrous acid is $C_5 H_2 O_3 = \bar{Ct}$; that of the hydrate $\bar{Ct}, HO$. It forms, like the preceding, both neutral and acid salts; and produces, with oxide of silver, a neutral salt with water of crystallisation; an apparently anomalous case. The formation of these two acids takes place as follows:—3 eq. of aconitic acid, $3\,(C_4 H_2 O_4)$ yield 2 eq. itaconic acid, $2\,(C_5 H_2 O_3, HO)$, and 2 eq. carbonic acid, $2\,CO_2$. The itaconic acid, when formed, is partially resolved into water and anhydrous citraconic acid.

The three acids just described, aconitic, itaconic, and citraconic acids, require further investigation. It is probable that it will be found that they are not all monobasic. The existence of water of crystallisation in the neutral citraconate of silver is a most unusual circumstance, and would seem to indicate that we do not yet know the constitution of the acid in that salt.

2. Tartaric Acid. $C_8 H_4 O_{10}, 2 HO = \bar{T}, 2 HO$.

This acid occurs in the juice of the grape as acid tartrate of potash ; also in many other plants. It is prepared from tartrate of lime, exactly as citric acid is from citrate of lime. Tartrate of lime is obtained by the action of chalk on acid tartrate of potash, or cream of tartar.

Tartaric acid crystallises in large rhombic prisms, transparent and colourless. They are very soluble in water, and have a pleasant acid taste. When boiled with alcohol, tartaric acid forms acid tartrate of oxide of ethyle. A high temperature decomposes tartaric acid, giving rise to several new products.

An excess of potash aided by heat, transforms it into acetate and oxalate of potash. $C_8 H_4 O_{10}, 2 HO = C_4 H_3 O_3, HO + 2 (C_2 O_3, HO)$. By peroxide of manganese and sulphuric acid it is converted into formic acid, carbonic acid, and other products. There is some relation between tartaric and formic acids : for if formic acid be FoO_3 ($Fo = C_2 H$), tartaric acid is $2 (Fo_2 O_5)$.

Tartaric acid precipitates lime-water white, but an excess dissolves the precipitate. In solution of potash, if the acid be added in excess, it causes a crystalline deposit of cream of tartar, which, where the potash is in very minute proportion, is rendered more visible by the addition of alcohol.

It is a bibasic acid, and forms two series of salts : 1. neutral $\bar{T}, 2 MO$; 2. acid, $\bar{T}, MO, HO$. It forms also two kinds of double salts : in one the 2 eq. of fixed base are different protoxides, $\bar{T}, \left\{\begin{matrix} MO \\ mO \end{matrix}\right.$; in the other, one of the equivalents of fixed base is replaced by 1 eq. of a sesquioxide; $\bar{T}, \left\{\begin{matrix} MO \\ m_2 O_3 \end{matrix}\right.$. This latter kind may be considered basic, since the sesquioxide, $m_2 O_3$, usually neutralises as much acid as 3 eq. of protoxide. Tartaric acid is remarkable for its tendency to form double salts.

Among the neutral tartrates are, *tartrate of ammonia* $\bar{T}, 2 NH_4 O + 2$ aq. ; *tartrate of potash*, or soluble tartar, $\bar{T}, 2 KO$; *tartrate of soda*, $\bar{T}, 2 NaO + 4$ aq. ; *tartrate of lime*, $\bar{T}, 2 CaO + 8$ aq., &c. &c.

Among the acid salts are, *acid tartrate of ethyle*, or tartrovinic acid, $\bar{T}, AeO, HO$—a crystallisable compound : acid tartrate of potash, or tartar, $\bar{T}, KO, HO$. This is the principal compound of tartaric acid. It exists in the juice of the grape, dissolved by the acid of the sugar present, and when that sugar is converted into alcohol, in which the tartar is insoluble, it is deposited on the sides of the fermenting casks. When purified it is quite white, and is called cream of tartar. It is much used in medicine as a safe and mild laxative. When calcined in a covered crucible it leaves a mixture of carbonate of potash and charcoal, called black flux. Hence carbonate of potash is called salt of tartar. Like all the tartrates, cream of tartar, when heated, gives off a very peculiar smell of burnt vegetable matter, peculiar to tartaric and racemic acids and their salts.

Among the very numerous double tartrates may be mentioned the *tartrate of potash and ammonia*, $\overline{T}, KO, NH_4O$: the *tartrate of potash and oxide of ethyle*, $\overline{T}$, AeO, KO; *tartrate of potash and boracic acid*, $\overline{T}, KO, BO_3$; this is the soluble cream of tartar used as a laxative on the continent:—*tartrate of potash and soda*. $\overline{T}, KO, NaO + 10$ aq. This is the salt of Seignette or Rochelle salt. It crystallises in very large transparent prisms, and is used as a mild laxative:—*tartrate of potash and peroxide of iron;* $\overline{T}, KO, Fe_2\,O_3$; this is the tartarised iron of the pharmacopœias:—*tartrate of potash and antimony*, $\overline{T}, KO, Sb_2\,O_3$. This is *tartar emetic*, one of the most valuable remedies. It must be considered as a basic salt; for $Sb_2\,O_3$, here substituted for HO or KO, in short for a protoxide, requires for its neutralisation an additional equivalent of tartaric acid. It then yields the compound $2\,\overline{T} + \left\{\begin{matrix}KO\\ Sb_2\,O_3,\end{matrix}\right.$ which is neutral, since the bases contain 4 eq. of oxygen for 2 eq. of acid.

Tartar emetic is formed when 3 parts of oxide of antimony and 4 of cream of tartar are ground together, and made into a thin cream with water, which is heated to 158°, till a portion, tried separately, dissolves in 15 parts of cold water. When this is the case, 6 or 8 parts of water are added, and the whole boiled for half an hour. The liquid, filtered while hot, deposits, on cooling, crystals of tartar emetic. It forms white brilliant crystals which soon become opaque. It is soluble in 14 or 15 parts of cold water and 2 parts of boiling water. The crystals are $\overline{T}, KO, Sb_2\,O_3, + 2$ aq.

When heated, the crystals first lose the 2 eq. of water of crystallisation; and when the heat rises to 390°, 2 more eq. of water are given off, without the acid being destroyed. The salt is then $C_8\,H_2\,O_{10} + \left\{\begin{matrix}KO\\ SbO\end{matrix}\right.$. That is to say, 2 eq. of oxygen, from the oxide of antimony, have been expelled along with 2 of hydrogen from the acid. It has been already shewn that tartar emetic, $C_{12} H_4 O_{10} + \left\{ \begin{matrix} KO \\ Sb_2 O_3 \end{matrix} \right.$ contains 2 eq. of oxygen in the bases, more than is required for a neutral salt; and it is apparently these 2 eq. of oxygen which are thus expelled as water. If we bear in mind that $Sb_2 O_3$ is the equivalent of 3 KO; or in other words, that Sb$\frac{2}{3}$ is equivalent to K or to H, we can then see that the tartar emetic heated to 390° is analogous in composition to neutral tartrate of potash.

$$\text{Tartrate of potash is} \quad . \quad . \quad C_8 \; H_4 \; O_{12} + K_2$$
$$\text{Tartar emetic, heated to 390° is,} \quad . \; C_8 \left\{ \begin{matrix} H_2 \\ Sb\frac{4}{3} \end{matrix} \right. O_{12} + \begin{matrix} K \\ Sb\frac{2}{3} \end{matrix}$$

In this point of view the 2 Sb are divided, $\frac{4}{3}$ Sb replacing hydrogen in the radical, and $\frac{2}{3}$ Sb replacing potassium in the base.

The *neutral tartrate of potash and antimony*, $2\,\bar{T}, \left\{ \begin{matrix} KO \\ Sb_2 O_3 \end{matrix} \right. +$ 7 aq. is always formed in the mother liquors of tartar emetic. It is also formed when tartar emetic is dissolved in tartaric acid.

Tartar emetic forms a double salt with cream of tartar, $\bar{T}$, $KO, Sb_2 O_3 + 3\,(\bar{T}, KO, HO)$. It crystallises in scales.

ACTION OF HEAT ON TARTARIC ACID.

When crystallised tartaric acid is heated it melts, then loses $\frac{1}{4}$ of its water, leaving a new acid, tartralic acid; next it loses $\frac{1}{2}$ its water, and is converted into tartrelic acid; and finally it loses all its water and is converted into anhydrous tartaric acid. We may represent these changes as follows, doubling the formula of tartaric acid.

$C_{16} H_8 O_{20} + 4\,HO =$ crystallised tartaric acid.
$C_{16} H_8 O_{20} + 3\,HO =$ tartralic acid.
$C_{16} H_8 O_{20} + 2\,HO =$ tartrelic acid.
$C_{16} H_8 O_{20} \qquad\qquad =$ anhydrous tartaric acid.

In tartralic and tartrelic acids, the neutralising power is diminished, in so far that tartralic acid neutralises $\frac{1}{4}$th less base, and tartrelic acid $\frac{1}{2}$ less base than tartaric acid. Both of these acids, as well as the anhydrous acid, are, by long boiling with water, reconverted into tartaric acid. It would appear as if in the tartralic and tartrelic acids, an additional quantity of anhydrous acid had been added to the radical without affecting the neutralising power, just as in phosphoric, pyrophosphoric, and metaphosphoric acids. If we represent the anhydrous acid by $C_4 H_2 O_5$, then we have

$2\,(C_4 H_2 O_5) + 2\,HO =$ crystallised acid.
$3\,(C_4 H_2 O_5) + 2\,HO =$ tartralic acid.
$4\,(C_4 H_2 O_5) + 2\,HO =$ tartrelic acid.

When tartaric acid, or rather anhydrous tartaric acid, is more strongly heated, it yields two pyrogenous acids, one liquid, the other crystallised. The former, $C_6 H_3 O_5, HO$, the latter, $C_5 H_3 O_3, HO$. In fact, 2 eq. of anhydrous tartaric acid contain the elements of 1 eq. of each of these new acids, 5 eq. of carbonic acid, and 2 eq. of water. The liquid acid is called pyroracemic acid, being obtained also from racemic acid: the solid acid may be called pyrotartaric acid.

Tartralic acid, $C_{12} H_6 O_5, 2 HO$, is obtained by cautiously heating tartaric acid, taking care not to cause it to become brown. It is combined with baryta, and the baryta separated from the soluble tartralate by diluted sulphuric acid. Tartralic acid forms a transparent mass, not crystalline, deliquescent and soluble in alcohol. It is converted into tartaric acid, slowly by cold water, rapidly by hot water. It appears to be bibasic, and most of its salts are soluble. By long contact with water, they are converted into tartrates and free tartaric acid.

Tartrelic acid, $C_{16} H_8 O_{20}, 2 HO$, is obtained by keeping the preceding acid long melted without raising the temperature. It is coloured brown, is deliquescent and dissolves both in water and alcohol. Water rapidly changes it into tartralic and tartaric acids. Its salts are soluble, and undergo the same change as those of tartralic acid.

Anhydrous tartaric acid, $C_4 H_2 O_5$, is prepared by rapidly heating ½ oz. of tartaric acid in a porcelain capsule. It swells up very much, gives off water, and is at last converted into a porous white mass. This is now heated for some time, in an oil-bath, to a temperature of 302°, then powdered and well washed with cold water, and dried. It forms a white powder insoluble in water, alcohol, and ether. By the action of water and bases it is converted successively into tartrelic and tartaric acids. —*Pyroracemic acid; or liquid pyrotartaric acid*, $C_6 H_3 O_5, HO = \overline{p}R, HO$, is one of the products of the distillation of tartaric and racemic acids. It is separated from the crystals which accompany it, combined with oxide of lead, and the well-washed pyrotartrate of lead decomposed by sulphuretted hydrogen. It is concentrated in vacuo, and forms a thick syrup nearly colourless, which cannot be distilled without partial decomposition. Its salts are not easily obtained in crystals, and when their solutions are heated, they lose the power of crystallising. The general formula of the pyroracemates is $C_6 H_3 O_5, MO$. They are coloured dark-red by salts of protoxide of iron, and a crystal of sulphate of copper introduced into the solution of a pyroracemate causes a white precipitate. *Pyroracemate of oxide of ethyle* is a colourless liquid, of an aromatic smell, resembling that of *acorus*.

Pyrotartaric acid, $C_5 H_3 O_3, HO = p\bar{T}, HO$, is formed along with the preceding acid in small quantity by the distillation of tartaric acid ; it is obtained far more abundantly by the distillation of cream of tartar. The product of the distillation, which is liquid, is evaporated till it crystallises, and the mother liquid, acted on by nitric acid to destroy the oily impurities, and again evaporated, yields an additional quantity. The crystals melt at 230° and volatilise at from 284° to 300°. The salts of this acid are soluble, that of lead appears to be rather sparingly so. But the results of different experimenters on this subject are so discordant that we must wait for further researches.

3. Racemic Acid. $C_4 H_2 O_5, HO = \bar{R}, HO$.

SYN. *Paratartaric acid.*—This remarkable acid, which has the same composition in 100 parts as tartaric acid, and very similar properties, is found along with tartaric acid in the grapes of certain districts. When both acids are present, the liquid obtained by boiling the tartrate and racemate of lime with diluted sulphuric acid deposits, on evaporation, racemic acid in hard crystalline crusts, before tartaric acid, which is more soluble, begins to crystallise. It may be distinguished from tartaric acid by not forming a double salt of potash and soda.

The crystals of the racemic acid have a very sour taste, and are composed of $\bar{R}, HO + aq$. At 212° they lose the 1 eq. of water of crystallisation, and when more strongly heated, yield the same products as tartaric acid. The solution of racemic acid forms a precipitate of racemate of lime when mixed with chloride of calcium, which serves to distinguish it from tartaric acid ; but like tartaric acid, it causes a crystalline precipitate in the salts of potash.

Racemic acid is monobasic, and for this reason does not, like tartaric acid, form double salts with two strong bases. It forms neutral salts, $\bar{R}, MO$, and acid salts, $\bar{R}, MO + \bar{R}, HO$. Thus the neutral racemate of potash is $\bar{R}, KO + 2\,aq.$, and the acid racemate of potash, analogous to cream of tartar, is $\bar{R}, KO + \bar{R}, HO$. These two salts, therefore, have precisely the same composition as the corresponding tartrates. The acid racemate of potash, with oxide of antimony, yields a double salt analogous to tartar emetic, but of a different crystalline form. The relations of racemic acid to the oxides of ethyle and methyle are similar to those of tartaric acid. On the whole, racemic acid is interesting, from its presenting one of the best marked cases of isomerism, namely, with tartaric acid. In this case, not only is the composition the same, but the general properties, and most of the special ones, are identical. In fact, were it not that we must admit tartaric acid to be bibasic, we should find it difficult to account for the differences which exist between the two acids. We have here a very near approach to the occurrence of different properties with the same composition, and even the same arrangement. The two acid salts of potash, for example, are $C_8 H_4 O_{10} \left\{\begin{matrix}KO\\HO\end{matrix}\right.$ for the bitartrate: and $C_4 H_2 O_5, KO + C_4 H_2 O_5, HO$ for the biracemate. If we represent the latter as follows: $\begin{matrix}C_4H_2O\\C_4H_2O_5\end{matrix}\left\{\begin{matrix}KO\\HO\end{matrix}\right.$, we see how very nearly alike they are, even on the view we have adopted of the one acid being bibasic, and the other monobasic; and we must bear in mind that these two salts are strikingly similar in properties. The same remarks apply to the crystallised acids and to the double salts with antimony, although in the case of the two acids, we have evidence of one point of difference in the arrangement. Tartaric acid is $C_8 H_4 O_{10}, 2 HO$, while racemic acid is $C_4 H_2 O_5, HO + aq.$, and loses the water of crystallisation at 212°.

4. Malic Acid. $C_8 H_4 O_8, 2 HO = \bar{M}, 2 HO$.

This acid is of very frequent occurrence in acid fruits, as in the apple, and especially in the unripe berries of *Sorbus aucuparia*, or mountain ash. The best method of extracting it is to express the berries when they begin to turn red, and to add to the strained liquid a thin milk of lime so as not entirely to neutralise the acid. On heating, neutral malate of lime is deposited and removed by a skimmer. To the mother liquid more milk of lime is added cautiously, so as to produce an additional quantity of salt. The malate of lime is washed with cold water, and dissolved with the aid of heat in a mixture of 1 part nitric acid, and 10 of water. On cooling, acid malate of lime is deposited in regular crystals, which are almost always colourless. They are rendered quite pure by a solution in hot water and crystallisation. From this salt, by the addition of acetate of lead, malate of lead is precipitated as a curdy white solid, which, if left in the liquid, changes into shining silky crystals. These, which are pure malate of lead, being decomposed by sulphuretted hydrogen, yield the acid, which when evaporated to a syrup forms a granular crystalline mass, deliquescent in the air, of a strong but agreeable acid taste. When the crystallised acid is kept for some time at a heat of 280° it melts, and the melted acid is gradually filled with crystals. Cold water removes the unchanged malic acid, which if again heated undergoes the same change, till at length all the malic acid is converted into these crystals, which are *paramaleic* or *fumaric acid.*

If malic acid be distilled by a sharp heat, a great part passes over in the form of a volatile crystallisable acid, the *maleic acid.* At a certain period of the distillation, if the retort be removed from the fire, the boiling residue having become turbid and thick, it suddenly becomes quite solid, and is found to consist of fumaric acid.

Malic acid is bibasic; in proof of which, it forms acid salts with lime, magnesia, and oxide of zinc, which monobasic acids never do. There are two series of malates: 1. neutral, $\bar{M}$, $2\,MO$; 2. acids, M, MO, HO. Most of the malates are soluble in water, but not in alcohol. Lime water neutralised by malic acid, continues clear whether cold or hot, which serves to distinguish it from tartaric, citric, racemic and oxalic acids.

Acid malate of ammonia, $\bar{M}$, $NH_4\ HO$, is best formed by neutralising with ammonia one of two equal portions of malic acid (as prepared from the crude malate of lead by diluted sulphuric acid), and then adding the other portion and evaporating to a syrup. On cooling, large and very regular crystals of the acid salt are deposited, which are easily decolorised by animal charcoal. This is an excellent method of purifying malic acid, when it is much contaminated with other substances. *Acid malate of lime* $\bar{M}$, $CaO, HO + 6$ aq., is prepared as above described. It forms very regular and pure crystals, soluble in their own weight of boiling water, but requiring 20 parts of cold water. When malic acid is saturated with chalk, an acid liquid is obtained, which, when boiled, deposits the *neutral* malate of lime, $\bar{M}$, $2\,CaO$. The *malate of lead* $\bar{M}$, $2\,PbO + 6$ aq. is remarkable for changing when left in the liquid in which it has been formed, from a curdy white precipitate to a mass of fine silky needles. In hot water this salt melts into a mass like pitch in consistence. *Acid malate of copper,* $\bar{M}$, $CuO, HO + 2$ aq. forms splendid large crystals of a fine cobalt blue colour. There appears to be a *basic malate of copper,* $\bar{M}$, $2\,CuO + CuO + 6$ aq., which forms green crystals. *Malate of silver,* $\bar{M}$, $2\,AgO$ is a white powder, soluble in boiling water. The other malates are analogous to these, and possess little interest.

Maleic Acid, $C_8\,H_2\,O_6$, $2\,HO = \bar{Ma}$, $2\,HO$, is prepared as above mentioned, by distilling malic acid. This acid is bibasic, but has the same composition, in 100 parts, as aconitic, or equisetic acid. It forms crystals, which are very soluble in water, alcohol, and ether. When heated sharply, it yields water, and a white volatile solid, melting at 134°, and boiling at 350°, which appears to be anhydrous maleic acid. When the hydrated acid is kept melted for some time, it is changed, exactly as malic acid is, into fumaric acid. Hydrated maleic acid has precisely the same composition as anhydrous malic acid, which at once explains its formation.

The general formula of its salts is $\overline{Ma}$, 2 MO for the neutral, and $\overline{Ma}$, MO, HO for the acid maleates. It forms an *acid maleate of silver*, $\overline{Ma}$, Ag O, HO.

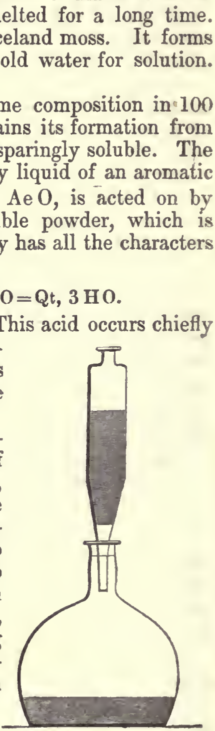
Fumaric or Paramaleic Acid, $C_4 HO_3, HO = \overline{Fu}, HO$, is formed as above stated, by heating either malic or maleic acids to their melting-point, and keeping them melted for a long time. It occurs in *fumaria officinalis*, and in Iceland moss. It forms micaceous scales requiring 200 parts of cold water for solution. It is soluble in alcohol.

It is a monobasic acid, but has the same composition in 100 parts as maleic acid, which at once explains its formation from malic, or from maleic acid. Its salts are sparingly soluble. The *fumarate of oxide of ethyle* is a heavy oily liquid of an aromatic smell of fruits. When this ether, $\overline{Fu}$, Ae O, is acted on by aqua ammoniæ, it forms a white insoluble powder, which is *fumaramide* $C_4 HO_2 + NH_2$. This body has all the characters of a compound amide.

5. Tannic Acid. $C_{18} H_5 O_9, 3 HO = Qt, 3 HO$.

SYN. *Quercitannic Acid. Tannine.* This acid occurs chiefly in oak-bark and in nut-galls, an excrescence on oak-leaves caused by the attacks of an insect which apparently pierces the leaf in order to deposit its eggs.

To obtain it, coarsely-powdered nut-galls are acted on, in an apparatus of displacement by ether, free from alcohol, but saturated with water. When the ether, after being left some time in contact with the powder, is allowed to drop into the lower vessel, it separates into two strata of liquid, the lower of which is a pure solution of tannic acid in water, which is drawn off and dried up after being washed with ether. The dry mass is redissolved in water, and again dried up in vacuo.



Tannic acid thus obtained is nearly white, and not at all crystalline. It is very soluble in water, and has a most astringent taste without bitterness. It is soluble in weak alcohol, but hardly soluble in ether. The aqueous solution, if exposed to the air, absorbs oxygen, produces an equal volume of carbonic acid, and is converted into *gallic* and *ellagic acids*. The addition of the mineral acids to a solution of tannic acid, causes a precipitate, which is composed of tannic acid and the acid employed (sulphuric, &c.), and which is very soluble in pure water. The precipitate formed by sulphuric acid, in a hot solution, dissolves in hot diluted sulphuric acid, and when this solution has been boiled a short time, it contains no tannic acid, the whole being converted into gallic acid.

Tannic acid combines with animal gelatine, forming an insoluble curdy precipitate. A piece of prepared skin, introduced into a solution of tannic acid, absorbs the acid, and is converted into leather. When heated, tannic acid is converted into metagallic and pyrogallic acids.

Tannic acid and its salts strike a deep blue, nearly black colour with persalts of iron; and it likewise causes a precipitate in the solutions of most of the vegetable bases.

It is a tribasic acid, and the general formula for the neutral tannates is $\overline{Qt}, 3\,MO$ in the case of protoxides, and $3\,\overline{Qt}, M_2O_3$, in the case of sesquioxides. These salts, however, have been but little studied.

The conversion of tannic acid into gallic acid is not fully understood. In some circumstances, it appears to depend on the absorption of oxygen; and in fact, 1 eq. tannic acid, *plus* 8 eq. oxygen, contains the elements of 2 eq. gallic acid, 4 eq. carbonic acid, and 2 eq. water. But when the conversion is produced by sulphuric acid, no other substance is formed with the gallic acid, except a colouring matter, which appears not to be essential. There is some probability that gallic acid exists ready formed in tannic acid, and if we subtract 2 eq. anhydrous gallic acid, $2\,(C_7\,H_2\,O_4)$ from 1 eq. of hydrated tannic acid, $C_{18}\,H_8\,O_{12}$, there is left $C_4\,H_4\,O_4$, which is the composition of hydrated acetic acid; or, tripled, that of dry grape sugar. As tannic acid, or at least the powder of nut-galls, if moistened, is said to be susceptible of the vinous fermentation, it is not impossible that tannic acid may contain gallic acid, *plus* sugar, if not gallic acid, *plus* acetic acid. Tannic acid is converted into gallic acid as rapidly by the action of an excess of alkali as by that of acid; but the whole subject requires investigation.

6. Gallic Acid. $C_7 HO_3, 2HO = \overline{G}, 2HO$.

This acid exists in the seeds of mango, and is formed as above described by the decomposition of tannic acid. It is purified from colouring matter by combining it with oxide of lead, and decomposing the gallate of lead, suspended in water, by sulphuretted hydrogen ; the sulphuret of lead acts as a decolorising agent.

Pure gallic acid forms beautiful prisms of a silky lustre, and a slight yellowish colour, of the formula $C_7 HO_3, 2HO + aq.$ It is sparingly soluble in cold water, requiring 100 parts, but dissolves in 3 parts of boiling water. Solutions of the acid and its salts, strike a black colour with persalts and proto-persalts of iron. When exposed to the air, the solution of gallic acid absorbs oxygen, and becomes dark-coloured ; this change is very rapid in the presence of alkalies, so that the alkaline gallates, especially if the alkali be in excess, are rapidly decomposed, and become nearly black.

When dissolved in hot oil of vitriol, and precipitated from the cold solution by water, gallic acid is obtained in a peculiar form, as $C_7 H_2 O_4$, perhaps $C_7 HO_3 + HO$, in which the crystals have lost 2 eq. of water, 1 basic or hydratic, the other, water of crystallisation. This peculiar gallic acid is a reddish-brown crystalline powder, which might be used in dyeing, as it yields colours on cloth like those from madder. When heated it forms fine red prisms, which call to mind alizarine, the crystalline matter found in madder.

By the action of heat, crystallised gallic acid yields, like tannic acid, pyrogallic and metagallic acids.

The gallates are little known. They are very easily decomposed by the action of the air. The *acid gallate of ammonia* is $\overline{G}, NH_4 O + \overline{G}, 2HO$. Acid gallate of lead has a similar composition. There is a bibasic gallate of lead, $\overline{G}, 2PbO$.

When tannic, or gallic acid, is heated by a sharp fire, carbonic acid, water, and *pyrogallic acid* distil over, while a dark solid remains in the retort, which is *metagallic acid.*

Pyrogallic Acid, $C_2 HO$? $C_6 H_3 O_3$? or $C_8 H_4 O_4$? forms shining scales of a bitter and astringent taste ; fusible at 240°, volatile at 410°. It is converted by a stronger heat into metagallic acid. It is formed from gallic acid, $C_7 H_3 O_5$, by the loss of 1 eq. carbonic acid. If acid at all, it is a very feeble acid, and nothing is known of its salts.

Metagallic Acid, $C_{12} H_3 O_3, HO$? $C_6 H_2 O_2$? is produced as above mentioned from tannic, gallic, and pyrogallic acids. It is a black powder, insoluble in water, soluble in alkalies. Of its salts little is known. It differs from gallic acid only by the elements of carbonic acid; $2 (C_7 H_2 O_4) = 2 CO_2 + C_{12} H_4 O_4$. From pyrogallic acid it only differs by the elements of water.

Tannic acid contains the elements of gallic and pyrogallic acids. $3 (C_{18} H_8 O_{12}) = 6 (C_7 H_3 O_5) + 2 (C_6 H_3 O_3)$; and since either gallic or pyrogallic acid may produce metagallic acid, it is obvious that there is a close connection among these four compounds. The precise nature of this connexion future experiments must ascertain.

When an infusion of nut-galls has been so long exposed to the air, that all tannic acid has disappeared, the gallic acid is found mixed with an insoluble, or sparingly soluble powder, which is a new acid, *ellagic acid*. Its composition is $C_7 H_3 O_5$, and when dried at 240° $C_7 H_2 O_4$; so that it is isomeric with gallic acid, and with the modified acid produced by the action of oil of vitriol. It has not been much studied, and we do not know its actual atomic weight. When heated, it yields greenish-yellow vapours, which condense into crystals of the same colour, insoluble in water, alcohol, or ether; soluble in sulphuric acid and in alkalies.

This acid is said to occur in the root of *Tormentilla vulgaris*.

Tannic acid, and the substances derived from it, occur in a good many plants, besides those of the genus *quercus;* the infusions of all of which are recognised by their striking a bluish-black with persalts of iron. But the astringent taste, and the property of tanning, or combining with animal gelatine, are found in many plants, such as cinchona, kino, catechu, pinus, &c. These are distinguished by giving, with persalts of iron, either a dark green or a gray colour. It has not been proved that they contain tannic acid, but Geiger has shown that these different colours may occur even when the same tanning principle is present, and that the green is owing, at all events frequently, to the presence of free acid, while the addition of chalk, in some cases, changes the green to the characteristic bluish-black due to tannic acid. There are, however, some reasons for admitting more than one tanning or astringent principle. The whole subject requires investigation.

Catechu. Mimotannic Acid.

When catechu, the dried extract of *mimosa catechu*, is acted on by cold water, it yields a soluble matter very similar to tannic acid, if not identical with it when pure. It is, however, contaminated by some compound which causes it to redden when exposed to air. It does not appear to yield the same products when heated, as tannic acid does; but this is uncertain, and may be caused by the presence of impurities. Berzelius proposes to call this tannic acid *mimotannic acid*, from *mimosa*, to distinguish it from the tannic acid of galls, which he calls *quercitannic acid* from *quercus*.

The portion of catechu insoluble in cold water contains a peculiar compound, called *catechine* or tanningenic acid. It is soluble in hot water, and when pure forms a white silky crystalline powder, which is said to be composed of $C_{15} H_6 O_6$. When heated, it is said to be transformed into (mimo ?) tannic acid. By the action of caustic potash it yields a black acid, *japonic acid*, $C_{12} H_4 O_4, HO$? Carbonate of potash converts it into a red acid, *rubinic acid*, $C_{18} H_6 O_9$ (?) in the anhydrous state. The hydrated acid is said to have the same composition as japonic acid, possibly therefore $C_{18} H_6 O_6$? But as the japonic acid, on the same authority, Svanberg, in combining with silver forms a salt $C_{24} H_8 O_8, AgO$, in which 2 eq. of the acid have lost 2 eq. of water and gained only 1 eq. oxide of silver, it is evident that our knowledge of these compounds is very imperfect.

7. Meconic Acid. $C_{14} H O_{11}, 3 HO = \overline{Me}, 3 HO$.

A tribasic acid, found only in opium, the dried juice of *papaver somniferum*. To prepare it, the crude meconate of lime, obtained in the manufacture of muriate of morphia, is mixed with 30 parts of boiling water, and 3 parts of strong hydrochloric acid added to the mixture, which must be removed from the fire, and not boiled after the acid has been added. On cooling, acid meconate of lime is deposited in shining crystals, which are collected on a cloth filter, squeezed, and treated a second time with the same quantities of acid and hot water. The strained acid liquid contains a large but variable proportion of sulphate of lime, always present, sometimes even to the extent of $\frac{1}{2}$ or $\frac{3}{4}$ in the crude meconate of lime. Hence the advantage of using so much hydrochloric acid, which also renders the meconic acid less soluble. This time the crystals are meconic acid, still much coloured. They are collected and squeezed as before, and to make sure that all lime is removed, a third time dissolved in 20 parts of hot water and 2 of hydrochloric acid. The addition of the acid not only removes the last traces of lime, but causes the meconic acid to crystallise almost entirely out of the liquid, it being nearly insoluble in diluted acid. The crystals, washed with a little cold water, and dried at the ordinary temperature, are now pure from everything but colouring matter, and when heated to redness leave no residue.

To get rid of the colour, the crystals are now mixed with warm water, and caustic potash gradually added, so as nearly but not quite to neutralise the acid. As soon as the point of neutralisation is reached, the reddish colour changes to green, and so much potash must be added that any further quantity would produce the green colour. The whole is then heated in the water bath, till all is dissolved, hot water being added, if necessary. (Were the potash now in excess, the whole acid would be decomposed into oxalic and carbonic acids.) On cooling, the meconate of potash, $\overline{\mathrm{Me}} \left\{ \begin{array}{l} 2\,\mathrm{KO} \\ \mathrm{HO} \end{array} \right.$ crystallises, forming a semisolid mass, which is to be squeezed out. The colour is carried off for the most part in the mother liquor, which is very dark, and the squeezed salt, after a second, or if necessary a third, solution in hot water, crystallisation, and squeezing, is snow-white. This purified meconate of potash is then acted on by pure hydrochloric acid, exactly as recommended for the meconate of lime, and after the third operation yields perfectly pure and white meconic acid in beautiful silvery scales, which, to remove any traces of the acid mother liquid adhering to them, may be once more dissolved in the smallest possible quantity of hot water, avoiding a heat of 212°, which decomposes the acid; the pure acid is deposited on cooling, as $\overline{\mathrm{Me}}$, $3\,\mathrm{HO} + 6\,\mathrm{aq}$.

Meconic acid, when gently heated, loses 6 eq. of water of crystallisation. It is soluble in water and in alcohol. When boiled, its solution becomes coloured, producing comenic acid, carbonic acid, and a dark-brown colouring matter. If boiled with hydrochloric acid, it is resolved into comenic acid and carbonic acid, without the production of colouring matter. When the dry acid is heated to 250°, the same change takes place. When heated with excess of aqua potassæ, meconic acid is entirely decomposed into oxalic acid, carbonic acid, and a dark colouring matter. Its distinguishing character is that of causing, in persalts of iron, a deep blood-red colour, but no precipitate.

It forms three series of salts, like other tribasic acids. Thus, there are three meconates of potash: 1. acid. $\overline{\mathrm{Me}}, \left\{ \begin{array}{l} \mathrm{KO} \\ 2\,\mathrm{HO} \end{array} \right.$; 2.

neutral, above-mentioned, $\overline{Me}\left\{\begin{matrix}2\,KO\\ HO,\end{matrix}\right.$ aq. Both of these crystallise. 3. tribasic, Me, 3 KO. This is yellow, and does not crystallise. There are also three meconates of soda; two of lime, acid and neutral or bibasic, and two of silver, bibasic $\overline{Me}$, 2 AgO, HO, and tribasic $\overline{Me}$, 3 AgO. The meconate of peroxide of iron is very soluble, of an intense blood-red colour, but as it cannot be obtained pure or crystallised, its composition is still unknown.

8. Comenic Acid. $C_{12}H_2O_8, 2\,HO = \overline{Co}, 2\,HO$.

This acid is formed as above described, from meconic acid by the action of heat, or of heat and an acid combined. 1 eq. dried meconic acid, $C_{14}HO_{11} + 3\,HO = C_{14}H_4O_{14}$, yields 1 eq. comenic acid, $C_{12}H_2O_8, 2\,HO$, and 2 eq. carbonic acid, $2\,CO\,2$. The acid is readily obtained by boiling meconate of lime with an excess of diluted hydrochloric acid. It is deposited on cooling in coloured crystals, which may be decolorised by recrystallisation with the aid of animal charcoal. The pure acid has a slight yellow tinge, and is very sparingly soluble in cold water. When heated, it is resolved into carbonic acid, *pyromeconic acid*, and a small quantity of a third substance, *paracomenic acid*, which, in some few points, differs from comenic acid, but has the same composition, and in many points is so similar that it may possibly turn out to be essentially the same.

Comenic acid forms two series of salts, with 1 and 2 eq. of fixed base respectively. With persalts of iron it forms a deep red solution which deposits black crystals, of unknown composition.

Pyromeconic Acid, $C_{10}H_3O_5$, HO, is obtained as a crystalline sublimate by heating meconic or comenic acids. In fact 1 eq. comenic acid, $C_{12}H_4O_{10}$ contains the elements of 1 eq. pyromeconic acid, $C_{10}H_4O_6$, and 2 eq. carbonic acid, $2\,CO_2$. It forms very soluble four-sided prisms, rather styptic to the taste; the solution of which forms with persalts of iron a crystalline salt of a fine red colour, the powder of which is like vermilion. This salt is $Fe_2O_3 + 3\,C_{10}H_3O_5$. Pyromeconic acid is so feeble an acid, that we can hardly class it with acids. It has more analogy with such bodies as acetone, derived from acetic acid, as pyromeconic acid is from meconic or comenic acid. It has the same composition as pyromucic acid.

9. Kinic Acid. $C_7H_4O_4, 2\,HO$? or $C_{14}H_{11}O_{11}, HO$?

This very remarkable acid occurs in cinchona bark. It is obtained in the manufacture of sulphate of quinine, in the form of kinate of lime, from which the lime is easily separated by means of oxalic acid. The liquid filtered from the oxalate of lime yields, on evaporation, the kinic acid in crystals. The lime may also be removed by sulphuric acid, and any adhering sulphate of lime separated by alcohol.

The salts of kinic acid are somewhat anomalous. Thus there is a salt of lead, $C_7\,H_4\,O_4\ 2\,PbO$, and a salt of copper, $C_7\,H_4\,O_4$, CuO, HO, while the crystals of kinic acid are $C_7\,H_6\,O_6$. All this would lead to the conclusion that the acid was a bibasic one, $C_7\,H_4\,O_4$, $2\,HO$. But the kinate of lime, and the kinate of silver, both quite neutral salts, are $C_{14}\,H_{11}\,O_{11}$, CaO, and $C_{14}\,H_{11}\,O_{11}$, AgO, as if the acid were monobasic, $C_{14}\,H_{11}\,O_{11}$, $HO = C_{14}\,H_{12}\,O_{12}$. If we assume the acid to be quadribasic, we can then bring all the above salts into one series.

Thus,—Kinic acid would be . $C_{14}\ H_8\ O_8,\ 4\,HO$

Kinate of lead . . . $C_{14}\ H_8\ O_8,\ 4\,PbO$

Kinate of copper . . $C_{14}\ H_8\ O_8,\left\{\begin{array}{l}2\,CuO\\ 2\,HO\end{array}\right.$

Kinate of lime . . . $C_{14}\ H_8\ O_8,\left\{\begin{array}{r}CaO\\ 3\,HO\end{array}\right. + 10\,aq.$

Kinate of silver . . $C_{14}\ H_8\ O_8,\left\{\begin{array}{r}AgO\\ 3\,HO.\end{array}\right.$

But the objection to this view is that, if this be the true constitution of the acid, the salts of lime and silver ought to be very acid, instead of being quite neutral.

PRODUCTS OF THE DECOMPOSITION OF KINIC ACID.

When kinic acid or kinate of lime is distilled with diluted sulphuric acid and peroxide of manganese, there is obtained a new compound called *kinone,* as a sublimate of fine golden yellow crystals, soluble in water, and very volatile, having a pungent smell in the state of vapour. Their composition is $C_{25}\,H_8\,O_8$. When acted on by reducing agents, it takes up 2 and 4 eq. of hydrogen, forming two new compounds, green and white hydrokinone. The *green hydrokinone,* $C_{25}\,H_{10}\,O_8$, is one of the most beautiful compounds known to chemists, forming long prisms of the most brilliant gold-green metallic lustre, surpassing those of murexide in beauty. It is best formed by adding a few drops of sulphurous acid to a solution of kinone. When an excess of sulphurous acid is used, the *white hydrokinone,* $C_{25}\,H_{12}\,O_8$ is formed, which crystallises in six-sided prisms. When acted on by oxidising agents, the solution of white hydrokinone becomes dark-red, nearly black, and almost immediately deposits the splendid crystals of the green compound. The latter is also formed by simply mixing solutions of kinone and white hydrokinone, being intermediate in composition between those bodies. Wohler, to whom we are indebted for most of our knowledge in regard to these very curious compounds, has described a series of bodies obtained from the above by the action of hydrochloric acid, chlorine, and sulphuretted hydrogen. The following tabular view contains the names and composition of these substances, as far as we yet know them.

Kinone	C_{25}	H_8	O_8	
Green hydrokinone . . .	C_{25}	H_{10}	O_8	
White hydrokinone . .	C_{25}	H_{12}	O_8	
Chlorohydrokinone . . .	C_{25}	$\left\{\begin{matrix}H_{10}\\Cl_2\end{matrix}\right.$	O_8	
Chlorokinone	C_{25}	$\left\{\begin{matrix}Cl_2\\H_6\end{matrix}\right.$	O_8	
Brown sulphohydrokinone . . .	C_{25}	H_{11}	O_7	S_4
Yellow ditto	C_{25}	H_{12}	O_7	S_5
Brown chlorosulphokinone . .	C_{25}	H_8 Cl	O_8	S_4?
Orange ditto	C_{25}	H_6 Cl	O_8	S_4?

It will be observed, that in all these formulæ the carbon remains unaltered, and that several are instances of pure substitution, as $C_{25}\,H_8\,O_8$ compared with $C_{25}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right.O_8$ and $C_{25}\,H_{12}\,O_8$, compared with $C_{25}\left\{\begin{matrix}H_{10}\\Cl_2\end{matrix}\right.O_8$. We can also see the relation of the sulphohydrokinones to kinone if we express them as follows:—$C_{25}\,H_8\left\{\begin{matrix}O_7\\S\end{matrix}\right.+3\,HS$; and $C_{25}\,H_8\left\{\begin{matrix}O_7\\S\end{matrix}\right.+4\,HS$.

We now come to a class of acids of very distinct and peculiar characters; those, namely, which occur as the chief constituents of fat oils and fats, vegetable or animal. Of these oily acids there are two kinds: 1. those which are volatile, and usually somewhat soluble in water; 2. those which have more character of the oils and fats from which they are derived, and can seldom be distilled without decomposition. We shall begin with the volatile oily acids.

10. Butyric Acid. $C_8\,H_7\,O_3$, HO.

This acid exists in small proportion in butter, in the form of a neutral *butyrate of glycerine*, or *butyrine*, to which the butter owes its peculiar and agreeable flavour. When butter is saponified by potash, and the solution of the soap is decomposed by tartaric acid, the oleic and margaric acids are separated as an oily stratum, while three or four volatile acids are dissolved in the water. These are butyric, caproic, capric and caprylic acids. The butyric acid may be extracted from the mixture; but it is far better obtained by the fermentation of sugar. When sugar, either cane, grape or milk sugar, is mixed with cheese, water, and chalk, and kept in a warm place, lactic acid is at first formed, which combines with the lime. But if the fermentation be continued at a pretty high temperature, 90° to 100° for example, the lactate of lime disappears, and is at last replaced by butyrate of lime. This salt is now distilled with diluted hydrochloric acid, and the distilled liquid treated with chloride of calcium, when it divides into two strata. The lighter is butyric acid, still containing water. It is rectified until the boiling point rises to 318°. The previous portions contain water; what now passes is pure.

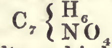
It is a clear, colourless, mobile liquid of an odour resembling that of acetic acid and that of butter. An intense cold solidifies it. It is very acid and corrosive. Its Sp. G. is 0·963. It dissolves fats and fat oils.

Chlorine decomposes butyric acid, producing by substitution two acids, $C_8 \left\{ \begin{matrix} H_5 \\ Cl_2 \end{matrix} \right. O_3, HO$; and $C_8 \left\{ \begin{matrix} H_3 \\ Cl_4 \end{matrix} \right. O_3, HO$. The latter crystallises; and both form volatile fragrant compounds with oxide of ethyle.

Butyrate of lime is remarkable as being very soluble in cold water, but separating from the liquid in transparent prisms when it is boiled. *Butyrate of baryta,* when placed on the surface of water, exhibits the same motions as camphor. *Butyrate of oxide of ethyle* or butyric ether, $AeO, C_8 H_7 O_3$, is formed with singular facility if a mixture of alcohol and butyric acid is distilled with the addition of a little sulphuric acid. It is a very mobile liquid of an odour somewhat similar to that of pineapples. It is very soluble in alcohol. This ether is employed to flavour spirits: and there is reason to believe that the peculiar flavour of rum depends on the presence of a little butyric ether. *Butyrate of oxide of methyle* is quite analogous. *Butyrate of oxide of glyceryle* or *Butyrine* exists in butter, and is supposed to be capable of being formed artificially, by warming a mixture of butyric acid, glycerine and sulphuric acid. If the oil thus formed is really butyrine, it will be the first example of a compound of glycerine formed or reproduced artificially.

Butyramide, $C_8 H_7 O_2 + NH_2$ is formed when liquid ammonia acts on butyric ether. $AeO, C_8 H_7 O_3 + NH_3 = AeO, HO + C_8 H_7 O_2, NH_2$. It crystallises in pearly scales.

Butyrone, $C_7 H_7 O$, analogous to acetone, is formed along with carbonate of lime, when butyrate of lime is distilled. $C_8 H_7$

$O_3, CaO = C_7 H_7 O + CaO, CO_2$. By the action of nitric acid, butyrone is converted into two new compounds; one, an ethereal fragrant liquid, lighter than water, the composition of which is not yet known: the other, an oily liquid, heavier than water, of an aromatic smell and a sweet taste, which is an acid, *nitrobutyric or butyronitric acid.* It is formed by substitution of NO_4 for H;  $C_7 \left\{ \begin{matrix} H_6 \\ NO_4 \end{matrix} \right. O, 2\,HO$ from $C_7 H_7 O$. It forms crystallisable salts, and is bibasic, yielding two salts with oxide of silver, with 1 and 2 eq. of that oxide respectively.

By distillation with perchloride of phosphorus, butyrone is converted into an ethereal liquid, chlorobutyrene, the composition of which is $C_{14} H_{13} Cl$.

The caproic, capric and caprylic acids found in butter, are very analogous to butyric acid, but are not yet so well known. *Caproic acid* is $C_{12} H_{11} O_3, HO$. Its odour is like that of sweat. *Caproate of oxide of ethyle* has an odour somewhat analogous to that of butter. *Capric acid* is $C_{20} H_{19} O_3, HO$. It is very analogous to the preceding, but its odour is more like that of the goat. *Caprylic acid* is $C_{16} H_{15} O_3, HO$, and it is very analogous to the others.

It occasionally happens that butter, instead of yielding a mixture of volatile oily acids, of which butyric and caproic acid constitute the principal part, gives a mixture devoid of these acids, but containing in their place another acid, vaccinic acid, which is easily transformed into the other two. There can be no doubt that it contains the elements of butyric and caproic acids, $C_8 H_7 O_3, HO + C_{12} H_{11} O_3, HO = C_{20} H_{20} O_8$ or possibly $C_{20} H_{19} O_7 = C_{20} H_{18} O_6, HO$. In the latter case, it would require 1 eq. of water to yield the other acids. As, however, the solution remains neutral when vaccinic acid passes into caproic and butyric acids, it is most probably bibasic, $C_{20} H_{18} O_6, 2\,HO$, and is, in fact, the sum of the other two. The cause of its occurrence is unknown.

Hircic Acid, the composition of which is unknown, is obtained from the fat of the goat, just as the preceding acids are from butter. It has an acid smell of goats, but is otherwise little known.

Phocenic Acid, $C_{10} H_7 O_3, HO$, is a volatile acid occurring in the blubber of the dolphin, and in the berries of *viburnum opulus.* It is extracted like the acids of butter, and is a liquid of a strong smell like that of rancid butter. It forms crystallisable salts with bases. It may possibly be the same as Valerianic acid.

Cevadic Acid is a crystalline volatile acid, obtained from the seeds of *veratrum sabadilla:* composition unknown.

Veratric Acid is contained in the same seeds. It is solid, crystallisable, and volatile. Its formula is $C_{18}H_9O_7, HO$. It forms a crystalline ether with oxide of ethyle; $AeO, C_{18}H_9O_7$.

Crotonic Acid is another solid volatile acid, found in the seeds of *croton tiglium.* It has a pungent, acrid taste, and a nauseous smell. It forms crystallisable salts.

11. Camphoric Acid. $C_{10}H_7O_3, HO = \bar{C}a, HO$.

This acid is formed by the action of nitric acid on camphor. It forms crystalline scales, sparingly soluble in cold water, very soluble in alcohol and ether, fusible at 158°. These are the hydrated acid, which, if distilled, is resolved into water and anhydrous camphoric acid. The camphorates are not peculiarly interesting. With oxide of ethyle, camphoric acid forms two compounds: 1. neutral, or *camphoric ether*, $\overline{Ca}, AeO$, an oily liquid, of a bitter taste and nauseous smell. 2. acid, $2\overline{Ca}, AeO, HO$, also called camphovinic acid, as it forms double salts, $2\overline{Ca}, AeO, MO$. When chlorine acts on camphoric ether, $\overline{Ca}, C_4H_5O$, it gives rise to the compound $\overline{Ca}, C_4 \left\{ \begin{matrix} H_3 \\ Cl_2 \end{matrix} \right. O$.

Anhydrous camphoric acid, $C_{10}H_7O_3$, forms, with bases, salts different from those formed by the hydrated acid. It is probable that it still retains some water replaceable by bases, being perhaps $C_{10}H_6O_2, HO$; or it may differ from ordinary camphoric acid as metaphosphoric acid does from common phosphoric acid. It is solid, crystalline, and volatile, and with dry ammonia forms a compound from which potash disengages no ammonia: with liquid ammonia it yields a salt different from camphorate of ammonia. Its action on oxide of ethyle has not been studied; but the subject deserves investigation.

It is worthy of notice that camphoric acid is isomeric with phocenic acid, and has apparently the same atomic weight. Qu.: Is one or the other bibasic?

By the action of sulphuric acid on anhydrous camphoric acid, there is formed, with disengagement of carbonic oxide, a new acid, *sulphocamphoric acid* $(C_9H_7O_3, SO_2)HO + 2$ aq. This acid is crystallisable, and forms crystallisable salts of the formula $(C_9H_7O_3, SO_2)MO = C_9H_7SO_5, MO$.

CAMPHOR.

There are two kinds of camphor: that of Japan, or common camphor, $C_{10}H_8O$; and that of Borneo, $C_{10}H_9O$, or $C_{20}H_{18}O_2$. The properties of common camphor, and its peculiar smell, are well known. Its Sp. G. is 0·985 to 0·996; it is very volatile, evaporating at ordinary temperatures. Small fragments of camphor, on the surface of water, evaporate more rapidly, with rotatory movements. It dissolves in alcohol, and is precipitated by water. When distilled with anhydrous phosphoric acid, it yields a carbo-hydrogen, called camphogen, $C_{20}H_{14}$.

When camphor is passed in vapour over a heated mixture of hydrates of potash and lime, it yields a new acid, *campholic acid*, $C_{20}H_{17}O_3, HO$. Nitric acid, with the aid of heat, converts camphor into camphoric acid. The *essence or oil of camphor* of commerce is $C_{20}H_{16}O = 2$ eq. camphor *minus* 1 eq. oxygen.

Borneo camphor occurs in small crystalline fragments. Its odour is different from that of common camphor. I find that, if wrapped in paper, a distinctly alliaceous odour traverses the paper, and may thus be detected. Heated with phosphoric acid, it yields a carbo-hydrogen, $C_{20}H_{16}$; and this is also the composition of the essence which accompanies Borneo camphor. This essence is, therefore, Borneo camphor, $C_{20}H_{18}O_2$, minus 2 eq. water.

Common camphor is produced by the *Laurus camphora;* Borneo camphor is the produce of *Dryobalanops camphora*, and is, for some unknown reason, so highly prized by the Japanese, that it is not found in the markets of Europe.

Camphogen, $C_{20}H_{14}$, is the name given to the carbo-hydrogen obtained when common camphor is distilled with dry phosphoric acid. It occurs naturally in the oil of cumin. When acted on by sulphuric acid, it forms a new acid, *sulphocamphic* or *hyposulphocamphic acid*, $C_{20}H_{13}S_2O_5, HO$.

When camphor is passed over red-hot lime, another new compound is formed, namely, *camphrone*, $C_{30}H_{21}O = 3(C_{10}H_8O) - H_3 + O_2$. At a white-heat camphor yields naphthaline, carburetted hydrogen, and carbonic oxide. 4 eq. camphor contain the elements ($C_{40}H_{32}O_4$) of 1 eq. naphthaline, $C_{20}H_8$; olefiant gas, $2\,C_4H_4$; marsh gas, $8\,CH_2$; and carbonic oxide, $4\,CO$.

12. Valerianic Acid. $C_{10}H_9O_3, HO = \overline{Va}, HO$.

This acid has already been mentioned as produced from hydrated oxide of amyle. It also occurs in the root of valerian. It forms two hydrates, $\overline{Va}, HO$, and $\overline{Va}, HO + 2$ aq.

The general formula of the valerates is $\overline{Va}, MO$. *Valerate of oxide of ethyle*, $\overline{Va}, Ae\,O$, is an oily liquid, of a smell like that of fruits and that of valerian at the same time.

By the action of chlorine, valerianic acid yields two new acids:

1. *Chlorovalerisic acid,* $C_{10}\left\{\begin{matrix}H_6\\Cl_3\end{matrix}\right. O_3, HO$. 2. *Chlorovalerosic acid,* $C_{10}\left\{\begin{matrix}H_5\\Cl_4\end{matrix}\right. O_3, HO$. Both these compounds are formed by substitution without change of type.

When valerate of lime is distilled, it is said by Löwig to yield a volatile oily compound, valerone, $C_9 H_9 O = C_{10} H_9 O_3 - CO_2$.

13. Anisic Acid. $C_{16} H_6 O_5, HO$.

This acid is obtained when the concrete essence of aniseseed is acted on by nitric acid. It is crystallisable and volatile, and forms salts which crystallise readily. When heated with an excess of baryta, it yields an oily liquid, called *anisole.*

The prolonged action of nitric acid on the concrete essence of anise produces another acid, *nitro-anisic acid,* in small yellow crystals. Its formula is $C_{16} H_5 NO_9, HO = C_{16}\left\{\begin{matrix}H_5\\NO_4\end{matrix}\right. O_5$, HO. It is now found to be identical with nitrodracinic acid.

Anisole, the product formed when anisic acid is heated with baryta, is composed of $C_{14} H_7 O_2 = C_{16} H_6 O_5, HO - 2 CO_2$. It is formed, also, when the salicylate of oxide of methyle is heated with baryta. By the action of bromine, anisole gives rise to two new products, in which 1 and 2 eq. of hydrogen are respectively replaced by bromine; $C_{14}\left\{\begin{matrix}H_6\\Br\end{matrix}\right. O_2$ and $C_{14}\left\{\begin{matrix}H_5\\Br_2\end{matrix}\right. O_2$. The latter is crystalline. Nitric acid acts violently on anisole, forming a crystalline mass, which dissolves in alcohol, with a rich green colour, but is deposited in colourless needles, corresponding to one of the bromine compounds. Fuming sulphuric acid dissolves anisole, producing two compounds; one, insoluble in water, analogous to sulphobenzine: the other, soluble, an acid analogous to sulphovinic acid. $2 SO_3 + C_{14} H_7 O_2, HO$.

Anisole, $C_{14} H_7 O_2$, contains 1 eq. of hydrogen more than hyduret of benzoyle, $C_{14} H_5 O_2, H$.

14. Œnanthic Acid. $C_{14} H_{13} O_2, HO$.

This acid, in combination with oxide of ethyle, forming œnanthic ether, is found in wine, in the oil of grain spirit, and in some other fermented liquors. It is, as œnanthic ether, the cause of that peculiar odour of wine which adheres so remarkably to vessels in which wine has been kept, and enables us at once to say that an empty bottle or cask has contained wine. To obtain the acid, the ether is decomposed by caustic potash, and the œnanthate of potash distilled with dilute sulphuric acid.

The hydrated acid is semisolid like butter, and is, in fact, a fat oil, insoluble in water, soluble in alcohol and ether.

Of its salts, the *œnanthate of oxide of ethyle*, œnanthic ether, is best known. It is a colourless liquid, of a peculiar vinous smell, which, when strong, has a stupefying effect. When hydrated œnanthic acid is distilled, it yields water, and anhydrous acid, more solid than the hydrate.

15. Roccellic Acid. $C_{17}H_{15}O_3, HO$?

This acid occurs in *Rocella tinctoria*. It is crystallisable, insoluble in water, soluble in alcohol and ether. It has most of the properties of a fat acid, and its salts with the alkalies resemble soaps.

16. Cuminic Acid. $C_{20}H_{11}O_3, HO$.

This acid is formed from the essential oil of cumin by oxidation with hydrated alkalies. It forms tabular crystals of singular beauty. It is fusible and volatile, insoluble in cold water, soluble in alcohol and ether. When heated with caustic baryta, it yields a carbo-hydrogen, analogous to benzole, which is called *cumene*.

It forms well-defined salts with bases. Cuminate of oxide of ethyle, formed by passing hydrochloric acid gas through a solution of cuminic acid in alcohol, is an ethereal liquid, of a fragrant smell like that of apples.

Cumene, obtained by heating cuminic acid with baryta, is a colourless liquid of a sweet smell. It is formed from cuminic acid, $C_{20}H_{12}O_4$, by the loss of 2 eq. carbonic acid, exactly as benzole is formed from benzoic acid; and its formula is consequently $C_{18}H_{12}$. Both nitric and sulphuric acid act on it and form new compounds, not yet fully examined. That formed by sulphuric acid is an acid, sulphocuminic acid, $C_{18}H_{11}, S_2O_5 + HO$.

Essence of cumin (*cuminum cyminum*) contains two oils: 1. Cuminole, $C_{20}H_{12}O_2$, which is the true oil of cumin, analogous to hyduret of benzoyle; 2. Cymene, $C_{20}H_{14}$, isomeric with camphogen. It is an oil of an agreeable odour of lemons. The oil is acted on by nitric and sulphuric acids, which produce two new acids. That formed with sulphuric acid is $C_{20}H_{13}, S_2O_5, HO$.

The *cuminole*, $C_{20}H_{12}O_2$, may be viewed as analogous to hyduret of benzoyle, in which case it becomes $C_{20}H_{11}O_2 + H$, the hyduret of a new radical, *cumyle*. Cuminic acid then becomes $C_{20}H_{11}O_2, O + HO$, analogous to benzoic acid. Chlorine acts on hyduret of cumyle, producing a compound, $C_{20}H_{11}O_2, Cl$, which is chloride of cumyle. Adopting the symbol Cm = $C_{20} H_{11} O_2$, we have CmH, CmO + HO, and CmCl, analogous to BzH, BzO+HO, and BzCl.

17. Eugenic Acid. $C_{20} H_{12} O_4$? or $C_{20} H_{13} O_5$?

This acid is found in cloves, along with a neutral oil, $C_{10} H_8$, or $C_{20} H_{16}$. The latter is separated by potash, and the eugenic acid obtained by distilling the salt of potash with dilute sulphuric acid. It is an oily liquid, of Sp. G. 1·079, having the strongest odour of cloves. It forms crystallisable salts with bases, and among them an acid salt of potash, $2 C_{20} H_{12} O_4 + KO + HO$?

Cloves, likewise, contain two crystallisable compounds: 1. *Caryophylline*, which forms yellow prisms; of the formula $C_{20} H_{16} O_2$, an oxide, therefore, of the neutral oil of cloves. 2. *Eugenine*, which forms yellow pearly scales, the composition of which is the same as that of eugenic acid.

18. Cocinic Acid. $C_{27} H_{26} O_3$, HO.

This acid, the first of the proper fat acids which we have come to, is found in the butter of the cocoa-nut combined with glycerine. The butter is saponified by potash, and the soap produced is decomposed by a mineral acid, when the fatty acid rises to the surface. It is purified by being again saponified, and finally by crystallisation in alcohol. It forms snow-white crystalline scales, fusible at 95°, and volatile. The salts of this acid with the alkalies are soaps like those of all fatty acids. *Cocinate of oxide of ethyle* is a colourless ether, with a very fragrant smell of apples.

19. Myristic Acid. $C_{28} H_{27} O_3$, HO.

This acid is found combined with glycerine, as a fat or butter in the berries of *myristica moschata* or nutmeg. There are two fats in the seeds, one red and unctuous, the other, myristine, white, and crystalline. It is easily purified by dissolving it in hot alcohol, in which it is, like the cocinate of glycerine, very soluble. On cooling, the pure myristine or myristate of glycerine is deposited as silky needles, which being saponified by potash, and the soap decomposed by an acid, yield myristic acid. The acid is purified by means of alcohol. It melts at 118°, and is decomposed by distillation.

The salts of this acid with the alkalies are soaps: very soluble in alcohol; and their aqueous solutions do not become viscid or ropy when concentrated. *Myristate of oxide of ethyle* is a colourless oil. Myristate of oxide of glyceryle or *myristine* is purified as above described. It is a beautifully crystalline fat, melting at 88°. It is saponified with difficulty, and only by fusion with solid potash. It does not appear to contain ordinary glycerine: at least its formula would indicate a glycerine composed of C_3H_2O. This point is at present very obscure.

The formula of hydrated œnanthic acid, doubled, or $C_{28}H_{28}O_6$, contains 2 eq. of oxygen more than 1 eq. of hydrated myristic acid, $C_{28}H_{28}O_4$; or the formula of dry œnanthic acid doubled, $C_{28}H_{26}O_4$, contains 1 eq. of hydrogen less and 1 eq. of oxygen more than dry myristic acid, $C_{28}H_{27}O_3$.

20. Palmitic Acid. $C_{32}H_{31}O_3, HO$.

This is the principal fat acid of palm oil. It is extracted by the usual process for fatty acids, and purified from oleic acid by crystallisation in alcohol. It forms brilliant scales, similar to margaric acid, and melting at the same point, 140°, as that acid. It may be distilled in great part unchanged. Chlorine decomposes it, giving rise to new compounds.

The salts of this acid with the alkalies are soaps, and palm oil is much used in soap-making. Palmitate of glycerine, or palmitine, is the fat or butter of the palm oil, purified from the oleine or liquid part, by pressure, and then by crystallisation in ether. It melts at 118°, and on cooling assumes the aspect of wax. Like myristine, it appears to contain the modified glycerine C_3H_2O, which is $\frac{C_6H_7O_5 - 3\,HO}{2}$; that is, glycerine, minus 3 eq. of water, and divided by 2. Pure palmitine (as also pure myristine), when distilled, yields *acroleine*, derived from the glycerine; but no sebacic acid. The crude palm oil, or impure palmitine, however, yields abundance of sebacic acid, a compound derived from oleic acid, and proving, therefore, the presence of oleic acid or rather oleine.

21. Cetylic Acid. $C_{32}H_{31}O_3, HO$.

Syn. *Ethalic Acid.* This acid, which is isomeric with the preceding, is formed when ethal (hydrated oxide of cetyle) is heated with hydrates of lime and potash. It is separated as usual in the case of fatty acids. It is a solid, fusible between 130° and 140°, and at 131° solidifying in radiated groups of needles. It may be distilled unaltered. Its salts are like those of the preceding acids.

22. Margaric Acid. $C_{34}H_{33}O_3, HO$; or, $C_{68}H_{66}O_6, 2HO$.

This is one of the most abundant and important of the fatty acids. Combined with glycerine, as margarine, it occurs in human fat and some other animal fats, and in many vegetable fats, such as olive oil. The acid may be extracted from soap made of these fats, but as it is mixed with much oleic acid, it is better to prepare it by oxidising stearic acid (see below) by nitric acid, or by distilling either tallow or crude stearic acid. In the latter case, the product is well squeezed and purified by solution in alcohol, and crystallisation. If prepared from pure stearic acid by nitric acid, it is pure from the first.

Margaric acid is a white solid fat, of distinct acid properties, fusible at 140°, very soluble in hot alcohol and in ether. It instantly combines with bases, decomposing the carbonates and forming perfect soaps with potash and soda. The neutral margarates of potash and soda are decomposed by the addition of much water, depositing the acid margarates in pearly scales. *Margarate of glycerine*, or *margarine*, is found pure in the solid part of human fat or of olive oil. It dissolves in hot alcohol, and crystallises on cooling. *Margarate of oxide of ethyle* is a white fusible solid.

The general formula of the neutral margarates is $C_{34}H_{33}O_3$, MO, or $C_{68}H_{66}O_6$, 2 MO. We cannot say with certainty whether margaric acid is unibasic, as the first of these formulæ would indicate, or bibasic, according to the second. We shall return to this point after describing stearic acid, and we shall also then describe the action of heat on both acids.

23. Stearic Acid. $C_{68}H_{66}O_5, 2HO = \overline{St}, 2HO$.

This is, perhaps, the most important and most abundant of the fatty acids. It exists, in combination with glycerine, as *stearine*, in beef and mutton fat, and in several vegetable fats, such as the butter of cacao. To obtain it, mutton suet is saponified by boiling with potash, and the purified soap decomposed by an acid, when a mixture of stearic and oleic acids, the latter in small proportion, rises to the surface. It is strongly pressed between warm plates, so as to get rid of the oleic acid in great part, and it is finally purified by solution in hot alcohol, and crystallisation, repeated till its melting point is constant at 167°. Or the stearic acid of commerce, which is nearly pure, may be purified by means of alcohol. Or again, tallow may be mixed with half its weight of oil of vitriol, and the mass melted in hot water, which removes a compound of sulphuric acid with glycerine, while the stearic acid rises to the surface and is to be purified as above. Finally, pure stearine, if saponified, and the soap acted on by an acid, yields at once pure stearic acid.

Stearic acid is a white solid, fusible at 167°, and on cooling forming brilliant white needles. It may be reduced to powder, and is, like all fat acids, insoluble in water, soluble in alcohol and ether. It burns like wax, and is used in the formation of improved candles.

By the action of nitric acid and other oxidising agents, stearic acid is at once converted into margaric acid, and it will be seen that the addition of 1 eq. oxygen is sufficient to effect this change. $C_{68}H_{66}O_5, 2HO + O = C_{68}H_{66}O_6, 2HO$.

Stearic acid is bibasic, and forms two series of salts; St, 2 MO, and St, MO, HO. The neutral stearates of the alkalies are perfect soaps. They dissolve in from 10 to 20 parts of hot water, and the addition of a large quantity of water decomposes them into acid stearates which are deposited, and basic stearates which remain dissolved. For the same reason a hot solution of a neutral stearate becomes gelatinous on cooling, from the separation of the acid salt. *Acid stearate of oxide of ethyle*, St, Ae O, H O, and *neutral stearate* of the same base, St, 2 Ae O, are both white crystalline fusible solids; as is likewise the *stearate of oxide of methyle*, St, 2 Mt O.

Stearine, the chief ingredient of suet and tallow, appears to be the *acid stearate of oxide of glyceryle*, but its precise formula cannot be determined as long as we are doubtful about that of glycerine. If glycerine be C_3H_2O, then stearine will be $C_{68}H_{66}O_5 + C_3H_2O + 2HO = \bar{St}$, Gly O, 2 HO; but if stearine be $C_6H_7O_5$, the formula will be $2(C_{70}H_{67}O_5)$ + Gly O + 2 HO; (using the older formula for stearic acid). Neither of these formulæ is satisfactory, as both exhibit 3 eq. of base and basic water, instead of two or four. When boiled with alkalies, stearine, like all other fats, is saponified: that is, the stearic acid combines with the alkali, forming soap, and glycerine is separated. Pure stearine is obtained by pressing tallow between hot plates, and afterwards dissolving in hot ether, which on cooling deposits the stearine. It is like wax in appearance when it has been melted, and it may be powdered.

Stearate of lead is an insoluble fusible soap, or, as it is called, a plaster. The same is true of margarate of lead, and in general of the compounds of lead with fat acids.

The composition of stearic acid stands in a very simple relation to that of margaric acid. If we call the compound $C_{34}H_{33}$, *margaryle*, and view it as a compound radical, representing it by the symbol Ml, then Ml_2O_5 = stearic acid and $Ml_2O_6 = 2\,Ml\,O_3$ = margaric acid. These acids, therefore, bear to each other the same relation as that which subsists between sulphuric and hyposulphuric acids, SO_3 and S_2O_5. The only difference is that, while SO_3 neutralises as much base as S_2O_5, $Ml\,O_3$ only neutralises half the quantity of base neutralised by Ml_2O_5, or in other words Ml_2O_6 neutralises as much base as Ml_2O_5.

When stearic acid is distilled alone, or with lime, it yields much margaric acid, and a neutral fusible crystalline fat, margarone, besides a solid carbohydrogen $C_{34}H_{34}$, carbonic acid, and water. Margarone is either $C_{33}H_{33}O$, or $C_{34}H_{33}O$. In the former case it is formed from margaric acid by the loss of 1 eq. carbonic acid; in the latter, it is the oxide of the supposed radical margaryle, Ml O. The production of these compounds is easily understood, for 2 eq. stearic acid are equal to 3 eq. margaric acid and 1 eq. oxide of margaryle; $2\ \text{Ml}_2\,O_5 = 3\ \text{Ml}\,O_3 + \text{Ml}\,O$. Again, 4 eq. of hydrated stearic acid contains the elements of 6 eq. hydrated margaric acid, 1 eq. margarone, ($C_{33}H_{33}O$), 1 eq. water, 1 eq. carbonic acid, and 1 eq. of the carbo-hydrogen $C_{34}H_{34}$. It would appear that according to circumstances the margarone has a different composition, its properties varying little, so that different chemists have obtained different margarones: namely $C_{33}H_{33}O$; $C_{34}H_{33}O$; and even $C_{68}H_{66}O = \text{Ml}_2O$. When margaric acid is heated, part distils unchanged, and part is converted into the above products.

When margarine or stearine are distilled, they yield the very acrid vapours of acroleine, a product derived from the glycerine contained in these fats; but pure stearic and margaric acids yield not a trace of acroleine. Neither do they yield any sebacic acid among the products of their distillation, this acid being derived exclusively from oleic acid.

ACTION OF NITRIC ACID ON MARGARIC ACID.

By the action of nitric acid stearic acid is converted into margaric acid, with disengagement of nitrous acid vapours. But if the action of the nitric acid be prolonged, the margaric acid is gradually oxidised and dissolved, being converted into *suberic acid*, *succinic acid*, and an oil soluble in nitric acid.

24. Suberic Acid. $C_8\,H_6\,O_3, HO = \overline{\text{Su}}, HO$.

This acid is formed when cork is oxidised by nitric acid, but especially when nitric acid acts on stearic acid, margaric acid, oleic acid, and other fatty bodies. The acid solution, obtained by boiling stearic or margaric acid with nitric acid till it is entirely dissolved, is evaporated to one half, and on cooling deposits a large quantity of suberic acid, which is easily purified by crystallisation.

It forms small granular crystals, fusible, when moist, at 130°, when dried, at 248°, volatile at a higher temperature, and subliming in the form of long needles. It is sparingly soluble in cold water, very soluble in hot water, in alcohol, and in ether.

The general formula of the suberates is $\text{Su}, \text{M O}$. The *suberate of oxide of ethyle* is prepared like the ethers of all the fatty acids, by passing hydrochloric acid gas through the alcoholic solution of the acid. When suberate of lime is distilled, it yields, among other oily products, a liquid boiling at 366°, the formula of which is C_8H_7O. It may be either the oxide of C_8H_7, or the hyduret of C_8H_6O. It is converted into suberic acid by the action of the air and of nitric acid. In fact, the addition of 3 eq. of oxygen gives the composition of hydrated suberic acid, $C_8H_7O_4$. It is probable that there exists a radical *suberyle* $= C_8H_6O = Su$; and that we have $Su\,H$, and $Su\,O_2, HO$ for the oil and suberic acid, analogous to the hyduret of benzoyle and benzoic acid.

25. Succinic Acid. $C_4\,H_2\,O_3, HO = \bar{S}, HO$.

This acid exists ready formed in amber, and may be obtained by distilling that body. But the mother liquor of the suberic acid, formed from margaric acid, &c., by nitric acid, contains a large quantity of succinic acid, along with a little suberic acid. The mixture, being dried up, is acted on by ether, which dissolves the suberic acid, leaving the succinic acid; it is finally purified by sublimation.

It forms regular crystals, which may be easily sublimed. The formula of the sublimed crystals is $2\,(C_4H_2O_3) + HO$; but by repeated sublimation it may be obtained anhydrous. The first hydrate $\bar{S}$, HO, melts at 356°, and boils at 455°, subliming, however, slowly at 284°. The sublimed hydrate, $2\,Su + HO$, melts at 320°, and boils at 468°; and the anhydrous acid melts at 257°, and boils at 482°.

By the action of anhydrous sulphuric acid, it yields a new acid, apparently $C_8H_2S_2O_{10}, 4\,HO$, hyposulphosuccinic acid.

The constitution of the succinates is still doubtful; but the most recent researches of Fehling, who has twice examined these salts with care, lead to the general formulæ of $C_4H_2O_3$, MO for the neutral, and $2\,(C_4H_2O_3) + MO, HO$, for the acid salts. The *succinates of lead* present some anomalies. By the action of ammonia, NH_3, on succinic ether, $C_4H_2O_3, C_4H_5O$, there is formed succinamide, $C_4\,H_2\,O_2, NH_2$, while alcohol, C_4H_5O, HO is given off. When acid succinate of ammonia is heated there is sublimed a new body, bisuccinamide, $C_8H_3O_4$, NH_2. It is formed from 2 eq. succinic acid and 1 eq. ammonia, by the separation of 2 eq. water. In their mode of formation these two bodies resemble oxamide and oxamic acid, only bisuccinamide has no acid properties.

The origin of *amber* is very uncertain; but it is most probably derived from some resin, formerly liquid or soft. It may possibly have arisen from the slow oxidation of a fatty matter, as we see succinic acid formed from fats by oxidation. Amber is a clear brittle yellow solid, becoming electric by friction. It is for the most part insoluble in all menstrua. When heated it yields succinic acid and a volatile oil, and there is left a large proportion of a matter which may be called bituminous, and forms the principal part of the amber.

26. Oleic Acid. $C_{44}H_{39}O_4, HO ? = \bar{Ol}, HO$.

This acid, in combination with glycerine, constitutes, as oleine, the liquid or most fusible portion of fats and fat oils. It exists in small proportion in tallow or suet; more abundantly in human fat and hog's lard; and it predominates in olive oil and especially in almond oil. To obtain it, almond oil is saponified, and the mixed fat acid obtained from the soap is digested with half its weight of oxide of lead, by which means margarate and acid oleate of lead are formed. Ether dissolves the latter only, and the ethereal solution of oleate of lead is acted on by hydrochloric acid, when the ether rises to the surface, holding the oleic acid in solution. The ether being distilled off, the oleic acid is left somewhat coloured. When pure it is a nearly colourless oily fluid, freezing in cold weather.

It forms salts with bases, and the oleates of the alkalies are soaps. Naples soap is chiefly oleate of potash: oleate of soda is harder.

Nitric acid converts oleic acid into suberic acid and other products. By hyponitric (nitrous) acid or nitrate of mercury it is converted into *elaidic acid.*

When distilled, oleic acid gives rise to sebacic acid, and this is an infallible test of the presence of oleic acid or oleine in any fat. This character applies to all the varieties of oleic acid, although we have reason to think that the oleic acids of fat oils and of drying oils are very different. Indeed, according to recent researches, the oleic acid of linseed oil is $C_{46}H_{38}O_5, HO$.

Of the oleates, the most important are those of potash and soda, which exist in most soaps, and constitute the chief part of those made with olive or almond oil, or whale oil, and that of lead, which is a valuable ingredient of most plasters. *Oleate of oxide of glycerile,* as already mentioned, is *oleine,* the liquid part of fats and fat oils, which is hardly known in a perfectly pure state. Oleate of oxide of ethyle is an oily liquid.

27. Sebacic Acid. $C_{10}H_8O_3, HO = \bar{Se}, HO$.

When any oil or fat, containing oleine or oleic acid, is distilled, and the product boiled with water, the hot filtered liquid deposits, on cooling, *sebacic acid* in small crystals resembling benzoic acid. It is soluble in alcohol and ether, and sublimes without alteration. The salts of sebacic acid are not remarkable, with the exception of the *sebate of oxide of ethyle*, which has a fragrant smell of melons. When we wish to ascertain the presence of oleine in a fat, a portion is distilled, the product is boiled with water, and the liquid, even if it deposit nothing, is tried by acetate of lead, with which it forms a white precipitate if sebacic acid be present.

28. Elaidic Acid. $C_{72} H_{66} O_5$.

This acid is formed by the action of nitrous acid on oleic acid. If a current of nitrous acid be passed through well-cooled oleic acid, the latter soon solidifies in large scales, which are *elaidic acid*. It is purified by solution in alcohol. It forms silvery scales, melting at 112°, very soluble in alcohol, and volatile without decomposition, except to a very small extent. The salts of this acid are soaps, and resemble those of the other fat acids.

Oleine is converted into *elaidine* (elaidate of glycerine), and oleic ether into elaidic ether, by the action of nitrous acid; but we cannot yet account for the production of elaidic acid in these cases or in that of its fermentation from oleic acid; since the reaction is accompanied by the production of other substances, not yet examined.

ACTION OF NITRIC ACID ON OLEIC ACID.

When oleic acid is acted on by nitric acid, it yields several acids, only one of which, suberic acid, occurs in the action of nitric acid on other fat acids. The remaining acids are, *azelaic acid? pimelic acid*, *adipic acid*, *lipic acid*, and *azoelic acid*.

The action of nitric acid on oleic acid is violent. When completed, the liquid is evaporated to one-half, and on cooling deposits suberic acid, which according to Laurent, is accompanied by azelaic acid, very similar to it, the composition of which he describes as the same as that of suberic acid, or only differing by 1 eq. of water, while he gives the formula $C_{10} H_8 O_4$, HO, that of suberic acid being $C_8 H_6 O_3$, HO. There is probably here an error of the press. But the existence of azelaic acid is very doubtful.

Pimelic acid crystallises on evaporation after the suberic acid has been removed, in hard granular crystals, fusible and volatile. Its formula is $C_7 H_5 O_3$, HO. In the mother liquid are found: —*Adipic acid* in round radiated masses, fusible and volatile. Formula $C_6 H_4 O_3$, HO (Laurent), $C_{14} H_9 O_7$, $2 HO$ (Bromeis), probably different acids. The *Lipic acid* forms long tables, very fine when formed in alcohol. Formula $C_5 H_3 O_4$, HO. *Azo-*

leic acid, according to Laurent, occurs in the form of an oily liquid, and œnanthic acid is also found. According to Bromeis, azoleic acid is doubtful, and the acid taken for it and for œnanthic acid is impure butyric acid, the formation of which is not improbable, since butyric acid contains exactly 1 eq. hydrogen more than suberic acid.

When oleic and elaidic acids are heated with potash there are produced acetic acid and a new fatty acid, $C_{32}H_{30}O_3$, HO. The difference between the formula of this acid and that of oleic acid is equal to 3 eq. acetic acid, which accounts for its production. Again, elaidic acid, $C_{72}H_{66}O_5$, *plus* 7 eq. oxygen, yields 2 eq. of the new acid, and 2 eq. acetic acid. This acid only differs from palmitic (ethalic) acid by 1 eq. hydrogen.

ACIDS OF CASTOR OIL.

Castor oil is a very peculiar oil. When saponified, it yields two fat acids, one crystallisable, *margaritic acid;* the other liquid, *ricinic acid.* The latter is little known. The former is said to be $C_{35}H_{31}O_6$. Castor oil is a mixture of the compounds of glycerine with these two acids. It is soluble, when pure, in its own bulk of alcohol. Nitrous acid converts it into a solid crystallisable fat, palmine, analogous to elaidine, but differing from it.

When castor oil is acted on by nitric acid, it yields a new volatile oily acid, of an agreeable aromatic odour, which is called *œnanthylic acid,* as its formula is that of œnanthic acid, *plus* 1 eq. oxygen; $C_{14}H_{13}O_3$, HO. It forms an ether of a very agreeable aromatic smell. In the residue is found suberic acid.

Palmine, the fat formed by the action of nitrous acid on castor oil, is a white crystalline fat, which when saponified, yields glycerine and a fatty acid, *palmic acid,* not yet fully investigated. A current of sulphurous acid passed through castor oil is said to produce palmine, or at all events a fat which yields palmic acid. This, if true, is a very singular fact, since nitrous acid, an oxidising agent, and sulphurous acid, a deoxidising one, would thus produce the same result.

NATURAL FATS AND FIXED OILS.

These are all compounds of glycerine with fatty acids. When heated with alkalies they yield soaps; with oxide of lead, plasters; while in both cases glycerine is set free. The most common of all these compounds are stearine, margarine, and oleine, of which always two, and often all three, are present, stearine predominating in the hard, margarine in the soft, and oleine in the liquid fats. It is only the compounds of glycerine with volatile acids, such as butyric acid, that have a strong smell.

There are two kinds of fat oils: the fat oils proper, and the drying oils. The latter contain much oleine, the oleic acid of which is different from the usual oleic acid, and they absorb oxygen from the air, drying into a kind of varnish. When oils become rancid, they are partly decomposed; and, generally, some of the acid, as well as of the glycerine, is set free, while oxygen is absorbed. Pure stearine, margarine, and oleine do not become rancid, and that change depends on a process of decay or slow oxidation going on in the impurities of the oil, and from them passing to the oil itself.

ACTION OF HEAT ON OILS AND FATS. ACROLEINE.

When oils are distilled they produce a variety of compounds, such as margaric acid, sebacic acid, margarone, carbohydrogens, &c. &c., and one most remarkable compound, *acroleine*, derived from glycerine.

Acroleine, $C_6H_4O_2$, is best obtained by distilling glycerine with phosphoric acid. The whole operations must be carried on in vessels full of carbonic acid gas, as the acroleine is very rapidly oxidised by the air. Its vapour attacks the eyes and nose in a most painful, indeed intolerable, degree. It may be considered as the hydrated oxide of a radical C_6H_3, (*acryle*, analogous to acetyle) $C_6H_3, O + HO$, analogous to aldehyde. It rapidly absorbs oxygen and forms *acrylic acid*, $C_6H_3O_3, HO$, analogous to acetic acid. In certain circumstances, the solution of acroleine exposed to the air, deposits a white solid, $C_{10}H_7O_4$.

The presence of acroleine among the products of the distillation of an oil or fat is a convincing proof of the presence of glycerine in that oil. It is worthy of remark that glycerine, $C_6H_7O_5$, is hydrated oxide of acryle, plus 3 eq. water, so that oils and fats may be called compounds of acroleine as well as of glycerine. It is even conceivable that acroleine may be C_3H_2O, which we have seen to be a probable form of glycerine in some fats; or that the glycerine in these fats may be acroleine, as above given, $C_6H_4O_2$, and that when this glycerine is separated by an alkali, it takes up 3 eq. of water.

Castor oil, so peculiar in other respects, exhibits a peculiar decomposition by heat. It yields acroleine, and a volatile oil, composed of two oils insoluble in alkalies; besides some saponifiable acids. When about one-fifth has been distilled, the residue suddenly consolidates into a spongy, yellow, elastic mass, insoluble in all menstrua except caustic alkalies, with which it forms peculiar soaps. These, when decomposed by an acid, yield a tough viscid substance having the characters of an acid. The product of the distillation again distilled with water, yields several oily compounds, one of which is crystalline, and not yet fully studied. The less volatile residue being again distilled yields a peculiar crystalline fatty acid, and another oily acid. Neither of these has been properly investigated.

When oils or fats are decomposed at a red heat, they yield much combustible gas (oil gas), formed of olefiant gas and marsh gas, and several liquid carbohydrogens: in particular benzole, $C_{12}H_6$, Faraday's quadricarboretted hydrogen, C_4H_4, or C_8H_8, and another isomeric compound, which is only liquid at very low temperatures.

ACTION OF SULPHURIC ACID ON FAT OILS.

Sulphuric acid, if added in small quantity to oils, combines with their glycerine; but if used in excess gives rise to a number of new products. In the first instance there are formed, when a mixture of oleine and margarine is acted on, two new acids, *sulpholeic acid* and *sulphomargaric* acid. These acids have not been isolated, but when their solution in water is heated, the sulphuric acid separates, and the oleic and margaric acids are transformed into four new acids, *metamargaric* and *hydromargaritic* acids, and *metoleic* and *hydroleic acids*. The two former are solid, crystallisable, and partly volatile. A compound of the two exists, which acts like a single acid and has been called *hydromargaric acid;* it is also a fusible solid. The two latter are oily, and all five appear to be bibasic. Their composition cannot be considered as ascertained, but the three first are nearly allied to margaric acid. It would lead to confusion here to mention the different formulæ proposed by Frémy, Berzelius, and Liebig, for these acids, more especially when it is considered that we have no sufficient evidence of the perfect freedom from foreign admixture of the acids analysed, and that the recent observations of Miller show an amount of variation in the melting points which leads to the suspicion of impurity. The subject is interesting, but difficult, and requires a very minute investigation.

Metoleic and hydroleic acids, when distilled, yield water, carbonic acid, and two carbo-hydrogens, *oleéne* and *elaéne*, both of which contain carbon and hydrogen in an equal number of equivalents; oleéne is supposed to be $C_{40}H_{40}$, and elaéne, $C_{45}H_{45}$; but this is not established.

ACTION OF NITROUS ACID ON FAT OILS.

Nitrous acid, or solution of nitrate of mercury, as already mentioned, causes fat oils to become solid, converting oleine into elaidine. This curious change takes place in olive oil, almond oil, rape-seed oil, hazel-nut oil, castor oil and others: but the drying oils, such as oils of linseed, hemp-seed, walnut, poppy-seed, &c., are not at all affected by nitrous acid. In all the oils which are changed into elaidine, except in castor oil, the product is the same. It is the formation of this solid fat which causes the mercurial ointments, made with nitrate, to become hard when kept. The elaidine, when purified by pressure and crystallisation in alcohol and ether, yields neither margaric nor oleic acid when saponified, but only elaidic acid. Hence, the elements of both the original acids have taken a share in the transformation. The conversion of oleic acid into elaidic acid by means of nitrous acid is accompanied by the formation of a red substance. The probable formula of elaidic acid is C_{70}, H_{68} O_6. As elaidine contains 2 per cent. more carbon than elaidic acid, it is plain that elaidine cannot be a compound of elaidic acid with a glycerine containing 5 eq. of oxygen to 6 eq. carbon. ($C_6 H_7 O_5$). It is therefore probable that elaidine is one of those fats in which the base is not ordinary glycerine but acroleine $C_6 H_4 O_2$, or $C_3 H_2 O$.

Castor oil, as has been already mentioned, yields, with nitrous acid, a new fat *palmine*, which contains a new acid, *palmic* acid. These resemble elaidine and elaidic acid, but are quite distinct.

ACTION OF BASES ON FAT OILS. SOAPS AND PLASTERS.

When fat oils are boiled with solution of caustic alkalies, they are gradually dissolved in the water, if there be not too great an excess of alkali present, forming ropy or gelatinous solutions, which gelatinise on cooling. These are solutions of soaps, that is, potash and soda salts of the fatty acids, along with the glycerine set free. In order to have the soaps in a solid form, the solutions are boiled down, and when the alkali reaches a certain concentration, the soap becomes insoluble, and rises to the surface in a soft, half melted state. This is drawn off into moulds, and the mass formed on cooling is soap. Another method of causing the soap to separate from the water in which it is dissolved, consists in adding sea-salt, which at once coagulates the soap, converting it into a soap of soda, if it is a soap of potash. Of course, the glycerine, in both cases, is carried off in the mother liquor. Such is the theory of soap-making, which is very simple, depending on the affinity between the alkalies and the fat acids; on the solubility in water of the alkaline stearates, margarates, oleates, palmitates, &c.; and finally on the power of a certain amount of free alkali or of sea-salt to coagulate the soap and render it insoluble in the liquid in which it swims, and which in fact, runs off its surface as water does off the surface of fat, while yet the soap retains perfectly its solubility in pure water.

The soaps of lime, baryta, &c. are insoluble in water, and have no detergent power: hence the waste occasioned by using hard, that is, calcareous, water for washing. All the salts of lime in such water must first be entirely precipitated in the form of curdy flocculi before any soap can be dissolved so as to act as a detergent.

The soaps of potash are soft, compared with those of soda, which are called hard soaps. White soap is stearate with some oleate, of soda. Naples soap is oleate and margarate of potash. Common soft soap is chiefly oleate of potash, but as it is made from whale oil or seal oil, it contains also phocenate of potash, which gives it a disagreeable smell.

Castile soap is oleate and margarate of soda, coloured by metallic oxides, chiefly oxides of iron, in such a way as to give the desired mottled appearance. Much and excellent soap is now made of palm oil, and is, therefore, palmitate of soda.

Soaps are soluble in alcohol, forming tincture of soap, which is an admirable liniment for bruises, and is much used along with laudanum, as tincture of soap and opium; also with camphorated spirit, forming opodeldoc.

Plasters are soaps of certain metallic oxides, chiefly oxide of lead, which are insoluble in water, but fusible, and possess useful properties. Litharge plaster is made by boiling finely 5 parts of powdered oxide of lead with 9 parts of olive oil and some water, till the combination is complete. It is plastic at ordinary temperatures, and melts when heated. When solution of acetate of lead is added to solution of soap, plaster, that is oleate and margarate of lead, is precipitated. When prepared in this way it becomes hard. White lead plaster, made with carbonate of lead, is very plastic and fusible, and is much used. Iron plaster and mercurial plaster are of small importance.

The chief liquid fat oils and drying oils of the vegetable kingdom have already been mentioned. In the animal kingdom, there are fish oils, characterised by containing phocenine; also cod liver oil, &c. &c.

The solid oils or fats of the vegetable kingdom, are butter of cacao (*theobroma cacao*); of nutmeg (*myristica moschata*); of cocoa-nut (*cocos nucifera*); of laurel (*laurus nobilis*); palm-oil (*Avoira elais: elais Guianensis*); galam butter (*Bassia butyracea*); and some others. Those of the animal kingdom are tallow, or suet, butter, hog's lard, human fat, &c.

Spermaceti is a peculiar fat found in the head of *physeter* *macrocephalus.* When purified from a small quantity of a liquid oil, it constitutes *cetine,* which is a compound of ethal (hydrated oxide of cetyle) with oleic and margaric acids. Cetine crystallises beautifully when melted or when dissolved in hot alcohol.

Cholesterine is a fat found in bile, and also, in small proportion, in the blood, and in much larger quantity as an ingredient of cerebral matter. It forms the chief ingredient of biliary calculi. It dissolves in hot alcohol, crystallises on cooling, in silvery scales, but cannot be saponified by boiling with potash. Its formula is either $C_{38} H_{33} O$, or $C_{36} H_{32} O$. When acted on by nitric acid, it yields a new acid, *cholesteric acid,* which contains nitrogen, probably as nitrous acid.

Ambreine, a fat analogous to cholesterine, is found in ambergris. It yields, with nitric acid, *ambreic acid.* Castorine is a similar fat found in castoreum.

Wax is another peculiar fatty body, the origin of which is derived from flowers, whence it is collected by the bee. It melts at about 150°. It is a mixture of two fats, *cerine* and *myricine,* the former soluble, the latter insoluble, in hot alcohol. Cerine is partly saponified, by boiling with potash, yielding apparently margaric and oleic acids (?) along with a neutral fat, *ceraine* having the same composition as myricine. There are several kinds of vegetable wax, but they are all much more easily saponified than bees' wax. When bees' wax is distilled, it yields neither acroleine nor sebacic acid, and would therefore appear to contain neither oleic acid nor glycerine.

Cerosine is the name given to a waxy substance occasionally found on the surface of the sugar-cane. It is not saponifiable, and appears to contain $C_{48} H_{50} O_2$.

Athamantine, from the root of *athamanta creoselinum,* is a crystalline fat-like body, containing valerianic acid, united to a body, *oreoselone,* which supplies the place of glycerine in the neutral athamantine. Oreoselone is $C_{14} H_5 O_3$, that is, isomeric with dry benzoic acid. Athamantine is $C_{24} H_{15} O_7 = C_{14} H_5 O_3$ (1 eq. oreoselone) $+ C_{10} H_{10} O_4$ (1 eq. valerianic acid). Athamantine combines with hydrochloric acid, and the compound, when boiled with water, deposits crystals, which are oreoselone *plus* water $= C_{14} H_6 O_4$, and isomeric with crystallised benzoic acid.

Having now briefly described the best known organic acids, it is necessary to mention a number of acids, found in the analyses of different vegetables, but not yet sufficiently studied to decide whether they exist independently or may not rather be, in many cases, identical with some of the acids above described.

Such are chelidonic acid, caincic, crameric, caffeic, boletic, fungic, tanacetic, lactucic, atropic, cocognidic, solanic, coneic, aceric, moroxylic, kinovic, and menispermic acids, besides others.

VOLATILE OR ESSENTIAL OILS.

These oils are so called because they are obtained by distillation of vegetables, generally along with water, and because, having, in most cases, the concentrated odour of the plant, they are usually called essences. Most of them exist ready-formed in the plant, which owes its smell to them: but some, as oil of bitter almonds and oil of spiræa, are formed by a kind of fermentation, excited in the case of the former, as already stated, by the contact of amygdaline, emulsine and water.

Many plants, when cut, yield balsams, which are mixtures of essential oils and resins. In many essential oils a crystalline matter is deposited, called a camphor or stearoptene. They are all soluble in alcohol. Many absorb oxygen from the air and become acid, as oil of cinnamon. They are violently acted on by nitric acid and iodine, chlorine, bromine, &c.

They may be divided into three kinds: 1st, those containing only carbon and hydrogen, as oil of turpentine. 2nd, those containing also oxygen, as oil of cloves. 3rd, those containing sulphur, as oil of garlic.

1. Non-Oxygenated Essential Oils.

Almost every one of these (which constitute a very numerous class of oils), as yet accurately analysed, has been found to contain carbon and hydrogen in the proportion $C_{10}H_8$, or what is the same thing, C_5H_4, or $C_{20}H_{16}$. The following are the most important.

Oil of turpentine, $C_{10}H_8$, or $C_{20}H_{16}$, is obtained by distilling, with water, turpentine, the juice exuding from many species of *pinus*. Rosin, resin, or colophonium, remains in the retort. The oil has a peculiar smell, and burns with a smoky flame. Its Sp. G. is 0·86. It boils at 312°. Strong nitric acid sets fire to it, and it is also decomposed with flame by chlorine. It dissolves sulphur, phosphorus, and fat oils. When exposed to hydrochloric acid gas, it combines with it, forming a white crystalline solid like camphor, and a liquid compound. The solid is $C_{20}H_{17}Cl = C_{20}H_{16}, HCl$. When heated with lime, it yields a pure oil, *dadyle*, $C_{20}H_{16}$. The liquid hydrochlorate, heated with lime, yields another pure oil, *peucyle*, rather more volatile than dadyle, but having the same composition. Oil of turpentine would seem to be composed of peucyle and dadyle, both $C_{20}H_{16}$; the former giving a liquid, the latter a solid compound, with hydrochloric acid.

Nitric acid, by long boiling, converts oil of turpentine into an acid, turpentinic acid. $C_{14}H_9O_7, HO$?

Oil of turpentine is used in medicine, internally, as a vermifuge, especially in cases of the larger worms, such as *tænia;* externally, as an excellent rubefacient and counter-irritant. In the arts it is much prized as a solvent for resins in making varnishes.

Oil of juniper has the same composition as oil of turpentine, but possesses its own peculiar odour, which it communicates to alcohol in *gin.* This oil is diuretic.

Oil of savine has the same composition. It is also diuretic. *Oil of elemi* has the same composition, and a pleasant odour. *Oil of storax,* or *styrole,* appears to have the composition of C_2H, or some multiple of it. Nitric acid acts on it, producing hydrocyanic acid, benzoic acid, and a fragrant crystalline body, nitrostyrole. Styrole itself is a very remarkable substance, differing as it does from all the other non-oxygenated oils. Dr. Blyth has been for some time engaged in its investigation, and has obtained very interesting results, not yet ready for publication.

Oil of lemons has the probable composition, C_5H_4. Like oil of turpentine it is composed of two isomeric oils, *citrene* and *citrylene,* which combine with hydrochloric acid, forming a liquid and a solid compound, decomposed by heating with lime. The solid camphor seems to be, $C_{10}H_9Cl = C_{10}H_8, HCl$. The oils of *cedro, cedrat, oranges, and limes,* are all essentially identical with oil of lemons. *Oil of neroli,* or of *orange-flower,* is quite distinct, having the odour of the flower, while the others have that of the rind of the fruit. Its composition is not accurately known.

Oil of copaiva is another isomeric form of oil of turpentine, which it very much resembles, forming a camphor with hydrochloric acid. It is diuretic, and much used in affections of the bladder and urethra. *Oils of pepper* and *of cubebs* are still of the same composition in 100 parts, although the latter is supposed to be $C_{15}H_{12}$.

2. Oxygenated Essential Oils.

The principal oils of this class have been already considered, their radicals being known. These are *oil of bitter almonds,* or hyduret of benzoyle ; *oil of spiræa,* or hyduret of salicyle ; *oil of cinnamon,* or hyduret of cinnamyle ; *oil of cloves* (eugenic acid) ; *oil of cumine,* or hyduret of cumyle ; *oil of aniseed,* the solid part of which is $C_{20}H_{12}O_2$, and with nitric acid yields anisic acid, and other compounds already described at p. 429 ; *oil of valerian,* chiefly valerianic acid, &c. The essence of valerian, according to Gerhardt, generally contains several compounds, especially if old. When fresh, it contains no valerianic acid, but an oil, *valerole*, which is crystallisable, and soon passes into valerianic acid in the air. This oil is $C_{12} H_{10} O_2$, and is isomeric with metacetone, also with Kane's oxide of mesityle, and with oxide of allyle (see oil of garlic, p. 451). Besides valerole, the essence contains a carbo-hydrogen, *borneéne*, $C_{10} H_8$, identical with the oil obtained from borneo camphor; and finally, a camphor, which is identical with borneo camphor.

Oil of cinnamon, according to Mulder, is, when quite fresh, $C_{20} H_{11} O_2$. It rapidly attracts oxygen, and $3 (C_{20} H_{11} O_2) + O_8 =$ 1 eq. cinnamic acid, 1 eq. resin alpha, $C_{12} H_5 O$, 1 eq. resin beta, $C_{30} H_{15} O_4$, and 6 eq. water $H_6 O_6$. With hydrochloric acid it yields two different resins, $C_{20} H_8 O$, and $C_{14} H_7 O$, besides other products. With oil of vitriol it yields two more resins, $C_{30} H_{15} O_2$, and $C_{30} H_{15} O$, which together are equal to 3 eq. of the oil *minus* 3 eq. water. With nitric acid the fresh oil forms a crystalline compound, $C_{18} H_9 N O_7 = C_{18} H_8 O_3 + N O_3 + H O$. With water this body yields hyduret of cinnamyle, $C_{18} H_8 O_2$. If dissolved in sulphuric acid and mixed with water it gives cinnamic acid, $C_{18} H_7 O_3$. Along with the crystals, nitric acid yields a red oil, which, with water, gives another oil, $C_{15} H_7 O_2$.

Oil of anise, $C_{20} H_{12} O_2$, yields with bromine a compound in fine crystals, $C_{30} \left\{ \begin{matrix} H_9 \\ Cl_3 \end{matrix} \right. O_2$. When acted on by strong acids, or by the chlorides of tin or antimony, oil of anise is converted into an isomeric body, anisoine, analogous to benzoine.

Of the remaining oils of this class may be mentioned the oils of *dill*, of *fennel*, of *parsley*, of *carraway*, of *coriander*, of *pimpernel*, of *peppermint* ($C_{10} H_{10} O$, or $C_{20} H_{20} O_2$; this oil yields several new compounds with chlorine), of *marjoram*, of *lavender*, *rosemary*, *basil*, *thyme*, *rue* ($C_{28} H_{28} O_3$), *cascarilla*, *chamomile*, *wormwood*, *tea*, *cardamom*, *nutmeg*, *cajeput*, *rhodium*, *rose* (otto or attar of roses), *bergamot*, *saffron*, *sassafras*, and *sweet bay* ($C_{20} H_{16} O$). Of these, little certain is known, and almost all require a careful study. The oil of sassafras, $C_{10} H_5 O_2$, when cooled, deposits very large and beautiful crystals, measuring 1½ inch on the side. With bromine, the solid essence yields crystals, composed of $C_{10} H Br_4 O_2$.

The oil or essence of *semen contra* is said to be $C_{18} H_{15} O_2$. That of *artemisia dracunculus*, or essence of estragon, yields, when treated with sulphuric acid, *anisoine*, identical with that of oil of anise, and in fact contains the same oxygenated oil (stearoptene of anise), along with a different carbo-hydrogen. Laurent has obtained from essence of estragon a series of new compounds. He represents the essence by $C_{32} H_{20} O_3$.

With nitric acid it yields draconic acid, $C_{32}H_{13}O_{10}, 2HO$; this, with chlorine and bromine, gives chlorodraconesic and bromodraconesic acids, $C_{32}H_{11}Cl_2O_{10}, 2HO$, and $C_{32}H_{11}Br_2O_{10}, 2HO$. Nitric acid yields further; $C_{32}\left\{\begin{matrix}H_{12}\\NO_4\end{matrix}\right.O_{10}$, $2HO$, which is called nitrodraconasic acid: and $C_{32}\left\{\begin{matrix}H_{11}\\2NO_4\end{matrix}\right.O_{10}$, $2HO$, which is nitrodraconesic acid. The former of these two acids, with chlorine and bromine, yields nitrochlorodraconesic acid, $C_{32}\left\{\begin{matrix}H_{11}\\Cl\\NO_4\end{matrix}\right.O_{10}\ 2HO$; and nitrobromodraconesic acid, $C_{32}\left\{\begin{matrix}H_{11}\\Br\\NO_4\end{matrix}\right.O_{10}$, $2HO$. With chlorine, the essence, $C_{32}H_{20}O_3$, gives chloride of draconyle, $C_{32}H_{15}Cl_7O_3$ (?), which, when acted on by potash, yields chloride of potassium and chlorodraconyle, $C_{32}H_{14}Cl_6O_3$. If formed by direct substitution, like the preceding compounds, the chloride of draconyle ought to be $C_{32}\left\{\begin{matrix}H_{15}\\Cl_5\end{matrix}\right.O_3$, the sum of the chlorine and hydrogen being 20 eq. as in the chlorodraconyle, in which, however, Laurent admits ½ eq. of hydrogen more. These researches of Laurent are very interesting; and it has very recently been established by Gerhardt and Laurent that draconic acid is identical with anisic acid, (p. 429), and that dracole, an oil obtained by heating draconic acid with baryta, is identical with anisole, (*ibid*). I presume that the true formulæ are those of draconic acid and its derivatives, so that the formula of anisic acid will have to be doubled.

The concrete essence of the tonka bean is called *coumarine.* It is very fragrant, and its formula is said to be $C_{18}H_7O_4$. Potash changes it into salicylic acid, and hot nitric acid converts into nitropicric acid. Cold nitric acid produces a white volatile crystalline solid, $C_{18}\left\{\begin{matrix}H_6\\NO_4\end{matrix}\right.O_4$. Coumarine also combines with chloride of antimony, forming yellow crystals.

3. Sulphuretted Essential Oils.

This class of oils is distinguished by a pungent peculiar smell, and acrid burning taste, as in oil of mustard, or an intense alliaceous odour, as in oil of garlic or of onions. The more important of them have been lately investigated, and have yielded very striking results.

Essence of mustard is prepared from mustard-seed in the same way as oil of bitter almonds from that seed. The seed is macerated with water and afterwards distilled, when it yields an oil of a most remarkable nature, containing not only sulphur, but also nitrogen. The pure oil is colourless, of Sp. G. 1·010, and boils at 298° or 300°. Its formula is $C_8 H_5 N S_2$, so that it contains no oxygen. With ammonia it forms a crystalline compound, which is, in fact, an organic base or alkali, *Thiosinnamine* $= C_8 H_8 N_2 S_2$. This is a bitter compound, which forms, like nearly all organic bases, crystalline compounds with chloride of platinum and chloride of mercury.

Thiosinnamine, acted on by dry oxide of lead or of mercury, loses all its sulphur, forming a new base, *sinnamine* $= C_8 H_6 N_2 = C_8 H_8 N_2 S_2 - 2 H S$. It is, therefore, Thiosinnamine, minus 2 eq. sulphuretted hydrogen, which have acted on the oxide of lead, forming water and sulphuret of lead. Sinnamine forms definite compounds with chlorides of mercury and platinum. It is a powerful base, and very bitter to the taste.

When oil of mustard is acted on by moist hydrated oxide of lead, it loses both sulphur and carbon, in the proportion CS_2, forming sulphuret of lead and carbonate of lead, along with a new base, *sinapoline,* which dissolves in hot water, in alcohol and in ether. Its formula is $C_{14} H_{12} N_2 O_2$; and it is formed from 2 eq. oil of mustard, with 6 eq. oxide of lead and 2 eq. water, as follows: $2 (C_8 H_5 NS_2) + 6 \text{PbO} + 2 \text{HO} = C_{14} H_{12} N_2 O_2 + 4 \text{PbS} + 2 (\text{PbO}, CO_2)$.

When oil of mustard is acted on by an alcoholic solution of potash, there is separated neutral carbonate of potash, and the addition of water causes the separation of an oily liquid, which is in its relations analogous to oil of mustard. It appears to be $C_{28} H_{25} N_3 S_4 O_4$. By the action of baryta upon it, sulphuret of barium is formed, and a basic compound not further examined. The liquid from which this oil has separated contains the potassium salt of a very remarkable acid, which forms with a salt of lead the compound $C_8 N H_6 S_4, \text{Pb}, = C_8 H_5 NS_2, HS + \text{PbS}$. These compounds are produced as follows: 6 eq. oil of mustard, 10 of water, and 2 eq. of potash, $6 (C_8 H_5 NS_2) + 10 \text{HO} + 2 \text{KO}$, yield 1 eq. of the new oil $C_{28} H_{25} N_3 S_4 O_4$, 1 eq. ammonia NH_3, 4 eq. carbonic acid, $C_4 O_8$, and 2 of the new salt of potassium $2 (C_8 H_6 NS_4, K)$. It is probable, however, that the first change is more simple, and that 3 eq. oil of mustard, 5 of water and 1 of potash, yield 1 eq. of an oil $C_{14} H_{14} N_2 S_2 O_2$, 2 eq. carbonic acid, $C_2 O_4$, and 1 of the potassium salt $C_8 H_6 NS_4, K$. Two eq. of the oil $C_{14} H_{14} N_2 S_2 O_2$ lose 1 eq. ammonia, and give rise to the oil $C_{28} H_{25} N_3 S_4 O_4$.

These very interesting facts, important in a high degree from their bearing on the theory of organic bases, are taken from a paper by Dr. Will lately published, to which I refer the reader.

Dr. Will points out some curious relations. Thus sinapoline, $C_{14}H_{12}N_2O_2$, may be derived from 2 eq. oil of mustard and 6 eq. water, which yield 1 eq. sinapoline, 2 eq. carbonic acid, and 4 eq. sulphuretted hydrogen. If we now suppose 2 of the 4 eq. of HS to combine with 1 eq. sinapoline, they will produce the oil, $C_{14}H_{14}N_2O_2S_2$, which is supposed to be first formed and afterwards to lose ammonia: while, if the 2 other eqs. of HS combine with 1 eq. of unchanged oil of mustard they will form the acid of the new potassium salt: $C_8H_5NS_2 + 2\,HS = C_8H_7NS_4$.

Again, sinapoline may be viewed as hyduret of benzoyle, *plus* 2 eq. ammonia, $C_{14}H_6O_2, 2\,NH_3$; and the hypothetical oil is then $C_{14}H_6O_2, N_2H_8S_2$, or hyduret of benzoyle, *plus* 2 eq. sulphuret of ammonium.

The separation of the elements of bisulphuret of carbon from oil of mustard, and the simultaneous formation of a series of basic compounds, would indicate that oil of mustard might be a compound of sulphocyanogen; since sulphocyanide of ammonium (see p. 312), when heated, gives off bisulphuret of carbon, and gives rise to a series of basic compounds, melamine, ammeline, &c. Now it is very remarkable that oil of mustard admits of being considered as $C_6H_5 + C_2NS_2$, that is, the sulphocyanide of a new radical *allyle*, C_6H_5; of which, as we shall presently see, oil of garlic is the sulphuret. Finally, oil of mustard may be a compound of hydrocyanic acid with the hydrosulphuret of sulphuret of acryle: $C_6H_3S, HS + C_2NH$. Its very pungent smell and powerful action on the eyes certainly rank it beside acroleine, C_6H_3O, HO. But all these views and relations are mentioned here as an example of the way in which such relations may be discovered, rather than as being in any way demonstrated.

Oil of mustard contains an indifferent nitrogenised body, *myrosine*, which, analogous to emulsine, yields the essential oil after maceration of the seed with water, and fermentation. The fermentation of myrosine is prevented in the same way as that of emulsine, namely by coagulation. The seeds also contain a crystalline body, *sinapisine*, resembling a fat. The substance, which, along with myrosine, yields the oil, appears to be *myronic acid*, or rather *myronate of potash*, a body not yet fully studied. The seeds of sinapis alba contain the myrosine, as sweet almonds contain emulsine; but, being destitute of myronic acid or myronate of potash, as sweet almonds are of amygdaline, they yield none of the oil.

It has very recently been shown, by Hubatka and Wertheim that the essential oils of cochlearia armoracia (horse-radish), cochlearia officinalis, and alliaria officinalis, consist almost entirely of oil of mustard, although the latter oil has also a very strong smell of oil of garlic, an oil which has not been discovered in it.

The essential oil of garlic, from the bulbs of *allium sativum,* is a peculiar sulphurised compound. Wertheim has lately studied it, and shown that it is the sulphuret of a new radical Allyle = $C_6 H_5$ = All, and its formula is $C_6 H_5, S$ = AllS. The crude oil contains a little of a higher sulphuret, possibly $AllS_2$, and also some of the oxide of allyle, $C_6 H_5 O$ = AllO, which is an oily liquid of an offensive smell. The radical allyle appears to enter into numerous combinations, and, among others, Wertheim analysed the following: the sulphuret, or pure oil of garlic, AllS; the compounds of that sulphuret with the sulphurets of platinum, palladium and silver, $5\ AllS + 6\ PtS_2$; $2\ AllS + 3\ PtS_2$; $2\ AllS + 3\ PdS$; and $x\ AllS + AgS$?; double compounds with the sulphurets and chlorides of mercury and platinum; $3\ (AllS + PtS_2) + (All\,Cl + Pt\,Cl_2)$; and $(AllS + 2\ HgS) + (All\,Cl + 2\ Hg\,Cl)$; and lastly nitrate of the oxides of silver and allyle, $(AllO + AgO) + NO_5$. Our space does not permit us to do more than point out the existence of these curious compounds.

The essential oil of *assafetida* appears to consist of at least two oils, one of which, if not both, contains sulphur. It has a very offensive odour. It does not combine with ammonia like the oil of mustard. Dr. Douglas Maclagan finds, as might be expected from the odour, that one of the oils it contains is sulphuret of allyle.

The essential oils of *hops,* of *water pepper,* and of *arum maculatum,* are believed to contain sulphur.

CONCRETE VOLATILE PRINCIPLES, ALLIED TO THE ESSENTIAL OILS.

There are several substances which may be classed under this head; such as *Hellenine* from *inula helenium,* which is a volatile crystalline solid, $C_{15} H_{10} O_2$. With nitric acid it yields *nitrohellenine* $C_{15} \left\{ \begin{array}{l} H_9 \\ NO_4 \end{array} \right. O_2$. When distilled with anhydrous phosphoric acid, hellenine loses 2 eq. water, yielding *hellenéne,* a carbo-hydrogen, $C_{15} H_8$. With chlorine it yields the compound $C_{15} \left\{ \begin{array}{l} H_9 \\ Cl \end{array} \right. O_2 + HCl$.

Asarone from *asarum europœum* is a volatile solid, having a remarkable tendency to crystallise in beautifully defined forms, and also to pass into the amorphous condition, from which it may be again brought into the crystalline state. Schmidt has very recently studied its crystallisation under the microscope, and has obtained results which are most interesting in reference to the formation of crystals in general. I must refer to his elaborate paper in the "Annalen der Chemie und Pharmacie," for February 1845. Its composition is, $C_{20} H_{13} O_5$

Anemonine, from various species of *anemone,* is a volatile, crystallisable solid, the formula of which is $C_5 H_2 O_2$. It forms with oxide of lead a compound, $3 (C_5 H_2 O_2) + PbO$. With bases it yields *anemonic acid,* the composition of which is unknown.

Cantharidine, the active principle of Spanish flies, is a volatile acrid solid, the composition of which is $C_{10} H_6 O_4$.

The following plants, *epidendron vanilla, quassia amara, tanghinia madagascariensis, primula auricula,* and *primula veris,* contain concrete volatile essences, not yet analysed.

CAOUTCHOUC, OR GUM ELASTIC.

Caoutchouc is a substance *sui generis,* which in composition approaches more nearly to the essential oils than to any other class of compounds. It is the coagulated or inspissated juice of many tropical trees, the chief of which is *siphonia elastica* (*iatropha elastica, hevea guianensis*). The juice, as it flows from the tree is made to dry on moulds of clay, which are afterwards broken out, leaving a bottle of caoutchouc. It is generally blackened by smoke, but when pure it is white and transparent, it is highly elastic, and the freshly cut surfaces adhere strongly if pressed together. It is insoluble in water, alcohol, and acids: but it dissolves in ether, naphtha, coal-tar naphtha, bisulphuret of carbon and essential oils. Its solutions in ether and coal-tar naphtha, when dried up, leave the caoutchouc in an elastic state. On this principle waterproof cloth is made. Caoutchouc is much used in chemical operations to form flexible connecting tubes.

When exposed to heat, caoutchouc first melts, and then distils, yielding a mixture of several oily liquids, all of which, as well as pure caoutchouc itself, are carbo-hydrogens. Some of these oils boil at 90°, others at 680°, and at intermediate points. I found that one highly rectified oil which boiled at 96°, and had the composition of olefiant gas, when acted on by sulphuric acid, yielded an oil which boiled at 428°, and had the same composition. But most of these oils have the composition of oil of turpentine, $C_5 H_4$ or $C_{10} H_8$. One of these, called *caoutchine,* gives with chlorine an oil, $C_{10} H_8 + HCl$.

RESINS.

Resins are generally found along with essential oils, and many of these oils, by the action of the air, are converted into resins. In this change, the essential oils lose a part of their hydrogen, which is converted into water, and take up some oxygen besides.

In fact, the resins, as a class, are acid bodies. They are insoluble in water, but become soft in boiling water. They dissolve in alcohol, and often crystallise from that solvent.

The acid resins combine with bases; their salts with the alkalies are called resinous soaps. The resins are not volatile, although very inflammable. They are purified from essential oils by distilling off the latter along with water; but, as thus obtained, they are generally mixtures of several resins.

Turpentine and *Colophony, or Common Resin.* Turpentine is the semifluid juice which exudes from many species of *pinus*. When distilled with water, it yields oil of turpentine, $C_{10}H_8$ or $C_{40}H_{32}$, while colophony or resin remains behind, which is $C_{10}H_7O$ or $C_{40}H_{28}O_4$, or, more accurately, $C_{40}H_{30}O_4$. Here the oil, $C_{40}H_{32}$, has lost 2 eq. hydrogen, replaced by 2 eq. oxygen, $C_{40}H_{30}O_2$, and this compound, like aldehyde, has taken up 2 eq. of oxygen to form the acid resin, $C_{40}H_{30}O_4$.

Colophony contains two different resins: resin *alpha*, or *pinic acid*, and resin *beta*, or *sylvic acid*. The latter is said to be $C_{20}H_{15}O_2$, the former $C_{40}H_{30}O_4$; and their properties are isomeric with it, very similar, being those of colophony which is formed of them. The sylvic acid is crystallisable.

When distilled with lime, colophony yields two oily liquids, *resineone*, $C_{26}H_{23}O$, and *resinone*, $C_{10}H_9O$.

The *resin of copaiva* is $C_{40}H_{30}O_4$, according to Rose; but there is some reason to believe that it is isomeric with the preceding. A variety of it has occurred, containing $C_{40}H_{30}O_8$, and when combined with oxide of lead, $C_{40}H_{28}O_6$. This resin crystallises.

The *resin of elemi* contains two resins, one crystallisable. Both are said to be $C_{20}H_{16}O_2$. *Anime* also contains two resins. *Euphorbium* yields a resin having the same composition as elemi. *Benzoin* contains, besides benzoic acid and a volatile oil, three resins, *alpha*, $C_{70}H_{42}O_{14}$; *beta*, $C_{40}H_{22}O_9$; and *gamma*, $C_{30}H_{20}O_5$. The resin alpha contains the sum of the other two, and by long boiling with carbonate of soda, which dissolves the resin gamma alone, is resolved into them.

Balsam of Tolu contains, besides essential oil, benzoic and cinnamic acids, and a carbo-hydrogen, $C_{24}H_{18}$, a resin, $C_{18}H_{10}O_5$. It contains the elements of benzoic ether, *plus* 1 eq. oxygen. When the balsam is distilled, *per se*, it actually yields benzoic ether, along with a new carbo-hydrogen, called benzoéne, $C_{14}H_8$. This last compound yields with sulphuric acid a new acid $C_{14}H_7S_2O_5 + 3HO$; and, with nitric acid, two new nitrogenised compounds, $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right.$, called *protonitrobenzoéne*, and another, binitrobenzoéne. The former is isomeric with salicylamide. With chlorine, benzoéne also yields several new products.

Styracine, the resin of styrax, is $C_{24}H_{11}O_2$. When acted on by nitric acid, it yields the products of decomposition of cinnamic acid.

The resin of guaiacum is remarkable for its tendency to become blue by the contact of many different substances. It contains two resins, but their composition is not ascertained. *Lac* contains four resins, besides colouring matter. *Dammara, mastic, dragon's blood*, and *sandarach*, are resins much used in making varnishes.

Jalap contains two resins; one, a soft resin soluble in ether, $C_{42}H_{34}O_{18}$; and an acid resin insoluble in ether, which, from striking a fine red colour with sulphuric acid, is called *rhodeoretine*, $C_{42}H_{35}O_{20}$. When combined with bases, it takes up 1 eq. water, forming *hydrorhodioretine*, very similar to rhodeoretine, but soluble in water, $C_{42}H_{36}O_{21}$. When rhodeoretine is acted on by hydrochloric acid, it is resolved into grape sugar, $C_{12}H_{12}O_{12}$, and an oily liquid *rhodeoretinole*, $C_{30}H_{23}O_8$. This reaction places rhodeoretine near to salicine and phloridzine. On the other hand, if we compare 7 eq. of starch, $7(C_{12}H_{10}O_{10}) = C_{84}H_{70}O_{70}$ with 2 eq. rhodeoretine, $2(C_{42}H_{35}O_{20}) = C_{84}H_{70}O_{40}$, we can see how this resin may be formed from starch, &c. by deoxidation. It is also worthy of notice that rhodeoretine agrees with salicine and phloridzine in the number of eqs. of carbon. Salicine is $C_{42}H_{29}O_{22}$ and phloridzine $C_{42}H_{29}O_{24}$. *Rhubarb* contains 3 resins, *aporetine, phæoretine*, and *erythroretine.* The two first are both $C_{16}H_8O_7$; the third is $C_{19}H_9O_7$. They are accompanied by an intensely yellow crystallisable acid, chrysophanic acid $C_{10}H_4O_3$ or $C_{40}H_{16}O_{12}$. This latter substance is also found in lichens, such as *parmelia parietina, squamaria elegans*, &c. *Copal*, which of all the resins is the most insoluble, is said to contain five. Copal varnish is made by adding hot oil of turpentine to copal fused at a gentle heat.

Turf or peat contains several resinous bodies, examined by Mulder. In the turf of Friesland he found 4 resins: *alpha*, $C_{30}H_{40}O_9$; *beta*, $C_{77}H_{67}O_9$; *gamma*, $C_{104}H_{94}O_9$; and *delta*, $C_{131}H_{121}O_9$. A lighter kind of turf from another locality yielded two resins; *alpha* $C_{35}H_{28}O_5$; and *gamma*, $C_{90}H_{84}O_6$.

Resinous varnishes are made by dissolving resins in oil of turpentine and other essential oils; or in drying oils. Spirit varnishes are made by dissolving resins in very strong alcohol.

ACTION OF HEAT ON RESINS.

When resins are distilled in close vessels, they yield a great deal of gas of a high illuminating power, and many volatile liquid compounds of carbon and hydrogen.

Pinic acid yields, when heated, *colopholic acid*. Colophony yields *resineine*, an oil, $C_{20} H_{15} O$; also *retinaphtha*, $C_{14} H_8$, which with chlorine forms a compound $C_{14} H_6 Cl_2$; *retinyléne*, $C_{18} H_{12}$, which with sulphuric acid yields an acid, isomeric with sulphocumenic acid, $C_{18} H_{11} S_2 O_5, HO$; *retinole*, $C_{32} H_{16}$; and finally a solid product, *retisteréne*, fusible at 152°, having the same composition as naphthaline, $C_{20} H_8$.

COLOURING MATTERS CONTAINING NO NITROGEN.

1. Yellow colouring matters.

The following are the most important of the yellow vegetable colouring matters, many of which are used in dyeing.

Curcumine, from the root of *curcuma longa*, is resinous, and is dissolved by alkalies, which change it to brown. Hence it is used as a test for alkalies, under the name of *turmeric*. *Gamboge yellow* is extracted from gamboge, the dried juice of *Garcinia gambogia*. It is resinous and powerfully purgative. *Annotto* or *Anatto* is obtained from the seeds of *Bixa orellana* and *Metella tinctoria*. *Carotine* is the colouring matter of the carrot, *Daucus carota*. *Rhabarberine* is a name formerly given to the yellow acid of rhubarb, now called *chrysophanic acid*, which is found also in lichens as above stated. It has great colouring power, and yields a fine violet with alkalies. It is fusible and volatile. Formula, $C_{10} H_4 O_3$. From occurring in *parmelia parietina*, it has also been called *parietine* and *parietinic acid*. *Luteoline*, the colouring principle of *Reseda luteola* or *Woad*, is volatile and crystallisable. *Quercitrine*, from the bark of *quercus tinctoria* is crystalline, and its composition is $C_{16} H_8 O_9, HO$. Other yellow colouring matters are *Morine*, from *Morus tinctoria*; *Safflower yellow*, from *Carthamus tinctorius*; *Polychroite* from *Saffron*, and others of less interest.

2. Red colouring matters.

Draconine, or Dragon's blood, is a red gum resin, from *Dracæna draco*. It is much used to colour varnishes. *Santaline*, the colouring matter of *pterocarpus santalinus*, is also resinous, and has an intense red colour. *Anchusine*, from *Anchusa tinctoria*, is the source of the colour of alkanet; it is resinous and yields violet vapours when heated. *Carthamine* is the red colouring matter of safflower, *carthamus tinctorius*. It is a very fine and intense red, much used for dyeing rose colour, for pink saucers and for rouge, at least the *rouge végétale.*

Madder, the root of *rubia tinctorum* contains three different red colouring matters, *madder purple, red,* and *orange*. All three are volatile, and the sublimed crystals of madder red, which are of a fine orange red colour, are called *alizarine.* This is the substance which yields the turkey red dye. With alkalies it yields purple or violet colour, with acids yellow. When dissolved in hot water or alcohol, alizarine yields rose-coloured solutions. The composition of pure madder red is unknown.

Hœmatoxyline is the red of *logwood, hamatoxylum campechianum.* It is soluble in water and alcohol, and yields orange crystals, which give to water a red colour, brightened by acids and turned to a violet or blue by alkalies. With alum, logwood yields various shades of violet ; with an iron mordant, grey and black. Black cloth and hats are dyed with it, which is the reason they are reddened by acids. According to Erdmann, pure hæmatoxyline is pale yellow, and is coloured red by the atmosphere. Its formula he found to be $C_{40} H_{17} O_{15}$. When acted on by ammonia it yields *hemateine*, which is dark red, and forms with excess of ammonia a splendid purple matter. Hæmateine is $C_{40} H_{15} O_{16}$; and the purple compound with ammonia is $C_{40} H_{15} O_{16} + 2 N H_3 + aq.$ *Brazilwood* and *Camwood* yield colouring matters very similar to hæmatoxyline, if not identical with it.

Many flowers contain a red colouring matter, which is turned green by alkalies, and is very fugitive. It is soluble in water and alcohol.

3. Blue colouring matters.

These are chiefly found in flowers and fruits. They are very closely allied to the red of flowers and fruits, which are no doubt often derived from them by the action of acids. They are all turned green by alkalies and red by acids. Such blue colouring matters as are more permanent contain nitrogen, and will be considered hereafter.

4. Green colouring matter. Chlorophylle.

This is the green of leaves. It is of a nature allied to that of wax, soluble in ether and alcohol, insoluble in water. It is very neutral or indifferent in its relations to other substances.

Polychrome is the name given to a peculiar crystalline principle found in some vegetables, such as quassia. It gives to water the quality of exhibiting a curious play of colours, among which blue predominates, like that of the opal, when the solution is viewed by reflected light, 1 part will give this property to 1,500,000 of water. Its formula is said to be $C_{16}H_8O_9, HO$, which is the same as that of *quercitrine*, and contains 2 eq. of oxygen more than the *aporetine* of rhubarb.

NON-AZOTISED VEGETABLE COMPOUNDS, THE NATURE OF WHICH IS NOT YET ASCERTAINED.

In this subdivision may be included a number of compounds, most of which crystallise and have a bitter taste, but are neutral and cannot yet be referred to any particular series of compounds. Salicine, phloridzine, and rhodeoretine, which would formerly have been here described, are now treated of along with substances allied to them. The substances now to be briefly mentioned have usually been termed the bitter and extractive principles of plants.

Gentianine, from *Gentiana lutea*, forms yellow needles, very bitter. *Menyanthine*, from *Menyanthes trifoliata*, is bitter, but does not crystallise. *Absinthine*, from *Artemisia absintheum* or wormwood, is a semi-crystalline mass, very bitter, soluble in alcohol. *Tanacetine*, from *tanacetum vulgare*, is very similar to it. *Santonine* is a beautifully crystallisable compound, obtained from *Artemisia contra*. It is soluble in alcohol, bitter to the taste, volatile, and coloured yellow by the action of light. *Populine*, from the bark and leaves of *populus tremula*, forms white crystals, of a sweetish and acrid taste, coloured red by sulphuric acid. It may possibly be connected with salicine. *Liriodendrine* is a crystalline bitter substance, from the bark of *liriodendron tulipifera*. *Picrolichenine* is an intensely bitter crystalline compound, found in the lichen *variolara amara*. It is principally febrifuge. In contact with ammonia and without the access of air, it is changed into a reddish-yellow matter, which finally deposits yellow crystals, not bitter. With access of air, it yields with ammonia a deep-red very soluble matter. *Cetrarine* is another bitter principle, from the lichen, *cetraria islandica*, or Iceland moss. It is coloured deep blue by hydrochloric acid. It is said also to be febrifuge. *Ilicine*, from *ilex aquifolium*, forms brownish-yellow crystals very bitter and febrifuge. *Syringine* is the bitter principle of the lilac, *syringa vulgaris*. It is crystalline and soluble in alcohol. *Daphnine* is a bitter crystalline substance, obtained from *Daphne Mezereon*. *Hesperidine* is a crystalline body found in the spongy envelope of oranges and lemons. *Elaterine* is the active principle of *Momordica Elaterium*, is crystalline, bitter, and very purgative. Its formula is $C_{20}H_{14}O_5$. *Colocynthine*, the active principle of colocynth, is amorphous, intensely bitter and purgative. *Bryonine*, from

Bryonia alba and *dioica*, is similar in its properties. *Mudarine* is the emetic principle of *calotropis mudarii.* It is a brown amorphous matter, the solution of which in water gelatinises at 95° and becomes again liquid on cooling. *Scillitine* is the bitter of *scilla maritima.* It is amorphous, bitter, purgative and emetic. *Cathartine* is the bitter purgative principle of senna. *Antiarine,* $C_{14} H_{15} O_5$, is the active principle of the poison called *upas antiar.* It is, when introduced into a wound, especially along with soluble matters such as sugar, a most powerful poison, and hitherto no means are known by which its fatal action can be arrested.

Zanthopicrine is a bitter crystalline substance from the bark of *Zanthoxylum Clava Herculis.* It has been little studied. *Picrotoxine,* the bitter principle of *menispermum cocculus* (cocculus indicus), forms white prisms. The composition of these is not certain, and recent researches seem to show that picrotoxine is a vegetable base, and contains nitrogen, like all that class of compounds. *Columbine* is a crystalline bitter substance, obtained from *columbo,* the root of *menispermum palmatum,* and somewhat analogous to picrotoxine. *Quassine* is a yellow, crystalline, and very bitter substance from the wood of *quassia amara.* Its formula is said to be $C_{20} H_{12} O_6$. *Lupuline,* the bitter principle of hops, is not crystallisable. *Lactucine* is a crystalline resinoid bitter substance, from the juice of *lactuca virosa* (lactucarium). It has anodyne properties. *Ergotine* is an uncrystallised brown powder, extracted from ergot of rye by hot alcohol, after the fatty matters have been removed by ether. It appears to be poisonous, and is probably the active matter of the ergot. *Porphyroxine* is a crystallisable substance found in Bengal opium. Its solution in diluted acids becomes red when boiled. It requires further investigation. *Saponine* is a peculiar principle, found in the root of *saponaria officinalis.* It is white, amorphous, and has a taste first sweet, then styptic, and finally acrid. It is a powerful sternutatory. It is soluble in water, and its solution, even when much diluted, froths when agitated, like a solution of soap. The root is used as a detergent. When acted on by alkalies, it is converted into an acid, saponic acid, $C_{26} H_{23} O_{12}$. *Asparagine,* $C_8 H_8 N_2 O_6, 2 HO$, is a crystallisable substance found in asparagus, in althæa officinalis, and in other plants, especially those grown in the dark. When boiled with alkalies it loses ammonia, $N H_3$, and forms *aspartic acid* $C_8 H_5 N O_6, 2 HO$, which is a bibasic acid. The crystals of asparagine are very large, colourless, and transparent, also hard and brittle. Not only alkalies, but acids, and ferments transform it into aspartic acid and ammonia. *Smilacine* is a crystalline substance, found in *smilax sarsaparilla.* Its composition is $C_{15}H_{13}O_5$. In *China nova* there is found a substance very analogous to smilacine, the composition of which is $C_{15}H_{12}O_4$: that is, smilacine, *minus* 1 eq. water. *Seneguine* is an acrid and astringent substance, found in *Polygala senega.* It excites sneezing powerfully. Formula, $C_{22}H_{18}O_{11}$. *Gaiacine* appears to be the active principle of guaiacum. It is acrid and bitter. *Plumbagine,* extracted from the root of *plumbago europœa,* forms yellow prisms, the taste of which is first sweet and styptic, then acrid and hot. The yellow colour of its aqueous solution is turned cherry-red by alkalies. *Cyclamine* is a crystalline matter from the root of *cyclamen europœum.* It is very acrid, purgative, and emetic. *Peucedanine* is a very acrid crystalline principle derived from the root of *peucedanum officinale.* Formula, C_4H_2O. *Imperatorine,* $C_{24}H_{12}O_5$, is a crystallisable compound, obtained from the root of *imperatoria ostruthium.* It is very acrid and styptic. *Phillyrine,* from the bark of various species of *phillyrea,* crystallises in silvery scales, which are bitter. *Fraxinine,* from the bark of *fraxinus excelsior,* is a crystallisable bitter principle. *Tanguine* is a similar substance from *tanghinia madagascariensis.* It is poisonous. *Melampyrine* is a tasteless, neutral, crystalline substance, from *melampyrum nemorosum.* *Meconine* is a neutral, crystalline compound contained in opium. It is soluble in water, alcohol, and ether. It is acrid to the taste, fusible, and volatile. Formula $C_{10}H_5O_4$. With nitric acid it yields *nitromeconine* or *nitromeconic* acid, $C_{20}H_9NO_{12}$. As meconine may be $C_{20}H_{10}O_8$, nitromeconine is $C_{20}\left\{\begin{matrix}H_9\\NO_4\end{matrix}\right.O_8$; in which 1 eq. hydrogen is replaced by 1 eq. nitrous acid. Chlorine transforms meconine into crystals containing chlorine, which, however, by the action of alkalies, yield an acid free from chlorine, mechloic acid, $C_{14}H_7O_{10}$?

Cubebine, $C_{34}H_{17}O_{10}$, is a crystalline compound contained in cubebs. *Olivile,* $C_{12}H_9H_4$, is a crystallisable acrid substance, found in the gum of the olive-tree. *Olivine* is another crystalline matter found on the leaves of the same plant. It is bitter. *Cnicine* is a crystalline matter, found in *centaurea benedicta,* and in the numerous family of the *cynarocephaleœ.* It is neutral and bitter, and very similar to columbine. Its formula is $C_{28}H_{18}O_{10}$, or $C_{42}H_{27}O_{15}$, and in some respects it approaches to salicine and phloridzine, which may render the second formula more probable, as these bodies contain 42 eq. carbon. *Limonine,* or *Limone,* a bitter crystalline matter found in the seeds of oranges, lemons, &c., is $C_{42}H_{25}O_{13}$, when reduced to 42 eq. carbon. This would be Cnicine, *minus* 2 eq. water. *Angelicine* is a crystallised compound found in angelica root.

Besides the above, which have merely been briefly catalogued for want of space, at least an equal number of substances, chiefly crystallisable, and either bitter, acrid, or in a few cases tasteless, have been extracted by various chemists from many different genera and species of plants, but have been so little examined hitherto that we cannot safely describe them as distinct and peculiar.

NITROGENISED COLOURING MATTERS, AND ALLIED SUBSTANCES.

There are several fine and valuable colours, which contain nitrogen as an essential element, and probably in the form of ammonia or amide. Such colours are *archil*, *litmus*, and *cudbear*, derived from certain species of lichens; and *indigo*, derived from the juice of various plants, especially different species of *indigofera*. All these colours are derived from colourless compounds, by the combined action of air and ammonia. Of these colourless substances, the most important are, *Lecanorine*, *Orcine* and *Erythrine*.

1. *Lecanorine* occurs in *lecanora tartarea*, *variolaria lactea*, and other lichens. It is extracted by ether, and forms minute white crystals, insoluble in water, soluble in alcohol and ether. Its formula is $C_{18} H_8 O_8$. When heated with alkalies, such as baryta, a carbonate is deposited, and a sweet substance remains dissolved, which crystallises on evaporation. This is *orcine*, $C_{16} H_8 O_4$, that is, lecanorine, *minus* 2 eq. carbonic acid, $C_2 O_4$. The same change takes place when lecanorine is boiled with water, or even with ordinary alcohol, and for this reason orcine alone is obtained when the lichens are extracted by these solvents.

2. *Orcine* forms large transparent crystals, is very soluble in water, and has a sweet taste. When anhydrous, it may be distilled unchanged. When mixed with ammonia, and exposed to the air, it gradually acquires a deep blood-red colour, forming a nitrogenised colouring matter, *orcéine*, soluble in ammonia with a deep red, in fixed alkalies with a rich violet colour. Crystallised orcine, $C_{16} H_{11} O_7$ ($C_{16} H_8 O_4 + 3 HO$) with the addition of 5 eq. of oxygen and 1 eq. of ammonia, NH_3, yields 1 eq. orcéine $= C_{16} H_9 NO_7$, and 5 eq. water, $H_5 O_5$.

3. *Erythrine* is another colourless substance, found in *Parmelia roccella*, when that lichen has been boiled with alcohol. It is probably a product of decomposition (just as orcine is) of some substance analogous to lecanorine. When exposed to the air along with ammonia, it slowly becomes red, and finally yields a

brown bitter compound, which dissolves in fixed alkalies with a purple colour.

4. *Pseudo-erythrine* is a similar substance, occasionally obtained, and occasionally altogether wanting, in the alcoholic solutions of the lichens. It is evidently subject to decomposition, when its solutions are boiled. Schunck has rendered it highly probable that it is a compound of lecanorine with oxide of ethyle.

5. *Variolarine* is a substance quite analogous to the abovementioned, and found in *variolaria dealbata*. The whole subject of the substances actually existing in these lichens is still very obscure. With the exception, perhaps, of lecanorine, all the above substances are products of decomposition. Even lecanorine may be a product of the decomposition of another substance, not yet isolated.

According to Kane, the following is the composition of

Erythrine (Erythriline, Kane) . . .	$C_{22}\ H_{16}\ O_{6}$
Pseudo-erythrine (Erythrine, Kane) . . .	$C_{22}\ H_{13}\ O_{9}$
Amarythrine (the bitter product) . . .	$C_{22}\ H_{12}\ O_{14}$
Telerythrine (a further product of oxidation) .	$C_{22}\ H_{10}\ O_{19}$

6. Archil contains, according to the same chemist, two blue compounds, which he calls *alpha-orcéine* and *beta-orcéine*, $C_{18}\ H_{10}\ N\ O_{5}$, and $C_{18}\ H_{10}\ N\ O_{8}$; besides a third of an acid nature, *erythroleic acid*, $C_{26}\ H_{22}\ O_{8}$.

7. Litmus contains (according to Kane) a red fluid, *erythroleine*, $C_{26}H_{22}O_{4}$; and three solids, of a purple colour, *erythrolitmine*, $C_{26}\ H_{23}\ O_{18}$; *azolitmine*, which contains nitrogen, and is the principal constituent of litmus; and *spaniolitmine*, $C_{18}\ H_{7}\ O_{16}$. According to Gélis, litmus contains three colouring matters, one soluble in ether, which is orange red; one soluble in alcohol, blood red, and one soluble in water. The second is the chief ingredient of the dye. All give blue compounds with alkalies.

8. *Phloridzéine* is the deep blue compound formed from phloridzine by the action of air and ammonia. Its formula is $C_{42}\ H_{29}\ N_{2}\ O_{26}$.

9. Indigo.

This valuable dye has been long known; but it is only since 1827 that its chemical relations have been accurately studied. No substance, in the whole range of chemistry, has yielded a greater variety of most interesting products; and the study of the metamorphoses of indigo has already thrown much light on the laws of the decomposition of organic substances. For what is known on this subject, we are indebted, first, in point of time, to Chevreuil, Runge, Walter Crum, Liebig, Berzelius, and Dumas; more lately, and in an especial manner, to the comprehensive researches of Erdmann, Fritzsche, and Laurent; the last of whom has made known several interesting series of new compounds derived from indigo, and has both confirmed and extended, as well as corrected, in some cases, the previous results obtained by Erdmann.

Indigo is obtained from various plants, chiefly of the genus *indigofera*, as *I. tinctoria*, *anil*, *argentea*, &c., but also of other genera, as *Nerium*, *Isatis*, *Pergularia*, *Gymnema*, *Polygonum*, *Tephrosia*, *Amorpha*, and others. In the juice of these plants, it exists in the form of a colourless soluble compound, probably a compound of white indigo with an alkali. When exposed to the air, it is converted into the blue compound, and becomes at the same time insoluble, just as in an artificial solution of white or reduced indigo in an alkali. The manufacture of indigo is not thoroughly understood, but it would appear that ammonia, as well as air, contributes to the formation of the colour, probably by converting into white indigo some compound present in the fresh juice, the nature of which, however, is still uncertain. In the Antilles and in the East Indies, the leaves are made to ferment in water, during which much ammonia is formed, and the indigo is found in the soluble state, ready to become blue and insoluble by absorbing oxygen. But in North America, the dried leaves are infused in warm water, or boiled with water, till the liquid becomes green, when, on exposure to the air, it deposits blue insoluble indigo. Here the same change must, in great part at least, have taken place during the drying, as during the fermentation of the other process.

The indigo of commerce is a deep blue powder, often cohering in cakes, and exhibiting, when polished by rubbing with the nail or any hard substance, a coppery colour and lustre. It is tasteless and inodorous, insoluble in water, and nearly so in alcohol and ether. It may be purified by treating it successively with boiling diluted sulphuric acid and with water, which remove a glutinous matter; with aqua potassa, at a gentle heat, which dissolves a brown colouring matter; and with boiling alcohol, which takes up a red colouring matter. When fresh alcohol becomes no longer red, but blue, the indigo is as pure as it can be made by such means.

To purify it still further, it is digested with water, lime, and grape or starch sugar, which deoxidises or reduces the indigo, while the lime combines with the reduced indigo, forming a soluble compound, of a wine yellow tint. This being filtered into dilute hydrochloric acid, which removes the lime, deposits pure indigo as a blue powder. Cloth steeped in the above solution of indigo, and exposed to the air, is quickly dyed blue, as the indigo, at the moment of being rendered insoluble, combines with the fibre of the cloth, to which it adheres very firmly, so that it cannot be washed away. If indigo, grape sugar, soda, and alcohol, be digested together in proper proportions, a yellow solution is obtained, which, when exposed to air, deposits pure indigo in crystals. (Fritzsche.)

Pure indigo, when rapidly heated on a slip of platinum, volatilises, yielding purple vapours, which condense in purple crystals on a cold surface. These crystals are called Indigotine: but they are nothing else than sublimed indigo, and have all the chemical characters of pure indigo. When distilled, indigo yields, among other products common to all nitrogenised organic matters, a very curious oily liquid, of powerfully basic properties, and forming salts with acids which crystallise with singular facility. This base is *aniline* (*crystalline, kyanol*), and is found in the oil of coal tar, as well as in the products of distillation of many nitrogenised bodies.

Oil of vitriol dissolves indigo with a deep blue colour, forming two blue acids. This solution is much used in dyeing. Nitric acid, chloric acid, chromic acid, chlorine and bromine, all dissolve indigo, giving rise to oxygenised and chlorinised or brominised products, all of which are yellow and orange-coloured. When boiled with strong aqua potassa, indigo is also oxidised and dissolved in the form of new acids.

When placed in contact with deoxidising or reducing agents, such as protosalts of iron, tin, and manganese, or honey and grape sugar, along with an alkali such as soda or lime, indigo is decolorised and dissolved in combination with the alkali. The addition of diluted hydrochloric acid, air being carefully excluded, precipitates *reduced* or *white indigo.*

White or reduced indigo, $C_{16}H_6NO_2$, obtained as above described, is a crystalline powder of a dirty white, which, if washed with water previously boiled to expel air, and cooled in closed vessels, and dried in vacuo, is blueish externally, but grey within. The blue parts being removed, the remainder is reduced indigo. When moist, it very rapidly passes into blue indigo, oxygen being absorbed: when dry, the change is more slowly effected. It is insoluble in water and acids, very soluble in alkaline solutions; its solutions, if exposed to the air, deposit pure indigo blue as a powder.

The first accurate analysis of indigo blue was made by Walter Crum; and his results have been confirmed by all succeeding experimenters. The formula now adopted for indigo, as agreeing best with its numerous metamorphoses, is one first proposed by Dumas; namely, $C_{16} H_5 NO_2$. This formula is the same with that of cyanide of benzoyle, or of benzile, $C_{14} H_5 O_2 + C_2 N = C_{16} H_5 NO_2$.

The relation of white indigo to blue indigo is, according to one view, the same as that of hyduret of benzoyle to benzoyle, or of alloxantine to alloxan. Thus we have

Benzoyle	$C_{14} H_5 O_2$	Hyduret of Benzoyle	$C_{14} H_5 O_2 + H$
Alloxan	$C_8 H_4 N_2 O_{10}$	Alloxantine . .	$C_8 H_4 N_2 O_{10} + H$
Indigo blue	$C_{16} H_5 N O_2$	Indigo white . .	$C_{16} H_5 N O_2 + H$

According to another hypothesis, white indigo is the hydrate of an inferior degree of oxidation of the same radical of which blue indigo is the higher oxide. Blue indigo, on this view, is $C_{16} H_5 N + O_2$, and white indigo is a hydrate $C_{16} H_5 N + O + HO$. This latter view is the more probable, not only in regard to indigo, but also in regard to alloxan, for, assuming *uryle* to be $C_8 N_2 O_4 = Ul$, alloxan will be $Ul + O_2 + 4 HO$, and alloxantine will be $Ul + O + 5 HO$.

The action of grape sugar, in reducing indigo, tells in favour of the latter hypothesis. For if white indigo is blue indigo *plus* hydrogen, this hydrogen is derived from water, the oxygen of which must have combined with the hydrogen of the sugar (to convert the sugar into formic acid, which is produced in this operation). Here, then, we should have oxygen leaving hydrogen to combine with hydrogen, or, in other words, water produced and decomposed at the same time, which is in the highest degree improbable. To demonstrate this, let the radical of indigo be assumed to be Anyle $= C_{16} H_5 N = An$: let blue indigo be $An O_2$, and white indigo $An O_2, H$ or $An O, HO$. Then 12 eq. of blue indigo, 12 of water, and 1 of grape sugar act on each other, and, according to the view which makes white indigo the hyduret of blue indigo, the reaction is as follows: $12 An O_2 + 12 HO + C_{12} H_{12} O_{12} = 12 (An O_2, H) + 6 (C_2 HO_3) + 6 HO$. In this explanation it is evident that 6 eq. of oxygen have quitted hydrogen to combine with hydrogen. On the other view, the reaction is as follows, free from any such absurdity: $12 An O_2 + 12 HO + C_{12} H_{12} O_{12} = 12 An O, HO + 6 (C_2 HO_3) + 6 HO$. Here the 12 eq. of deutoxide of anyle (blue indigo) lose 12 eq. oxygen, which are replaced by 12 eq. water; and the 12 eq. oxygen acting on the sugar, 6 eq. take 6 eq. hydrogen, forming water, and 6 eq. convert the residue into formic acid. The student will bear in mind that $C_2 HO_3$ is the formula of formic acid, and $C_{12} H_{12} O_{12}$ that of dry grape sugar.

We shall therefore consider white indigo as the hydrated protoxide of anyle ($C_{16} H_5 N, O + HO$), and blue indigo as the anhydrous deutoxide ($C_{16} H_5 N, O_2$). White indigo forms compounds with bases, in which, no doubt, its hydratic water is replaced by an equivalent of metallic oxide, as in the general formula, $C_{16} H_5 N, O + MO$.

ACTION OF SULPHURIC ACID ON INDIGO.

When powdered pure indigo is added to 15 parts of oil of vitriol, and gently warmed, a deep blue solution is formed, which mixes perfectly with water. But if only 8 or 10 parts of acid are used, the addition of water causes the deposition of a purple powder, while a blue solution is obtained. The purple powder, which, although insoluble in dilute acid is soluble in pure water, is sulphopurpuric acid; the blue solution contains two acids, sulphoindigotic and hyposulphoindigotic acids. When neutralised with potash, these acids form salts, which separate from the liquid when it is saturated with any alkaline salt, such as acetate or carbonate of potash. The two blue salts may be separated from each other by alcohol, but the composition of the hyposulphoindigotate of potash is not known. The sulphoindigotate appears to be strictly a hyposulpho-indigotate, and its formula is in all probability $C_{16} H_4 NO_2, S_2 O_5 + KO$. Here the indigo has lost 1 eq. of hydrogen, and the 2 eq. sulphuric acid 1 eq. oxygen. Dumas's view, according to which the salt is a double sulphate, analogous to sulphovinate of potash, $C_{16} H_4 NO, SO_3 + KO, SO_3$, is not supported by the chemical relations of these substances. Dumas conjectured that indigo blue was analogous to alcohol, and that its formula was $C_{16} H_4 N, O + HO$, the body $C_{16} H_4 N, O$ being analogous to oxide of ethyle. But, as already stated, this view is far-fetched, and does not agree with the chemical relations of indigo. It would make, for example, white indigo $C_{16} H_4 N, O + H + HO$ or $C_{16} NH_4 + 2 HO$, both most improbable formulæ.

The blue solution of indigo in oil of vitriol, if diluted and digested with flannel or woollen cloth, is entirely deprived of blue colour, while the cloth is so effectually dyed that the colour cannot be washed out. It can, however, be dissolved from the cloth by carbonate of ammonia, and by this means the sulphoindigotates of ammonia, and from these, the other salts of the blue acids, are prepared.

The sulphopurpuric acid, according to Dumas, contains the elements of 2 eq. sulphuric acid and 2 eq. indigo, and neutralises only 1 eq. of base. But the indigo in it has probably lost hydrogen (while the acid has lost oxygen), or hydrogen and oxygen.

PRODUCTS OF THE OXIDATION OF INDIGO.

Isatine, $C_{16}H_5NO_4$. This interesting compound, which is blue indigo, *plus* 2 eq. oxygen, is formed by digesting indigo along with water, sulphuric acid, and bichromate of potash, or by heating indigo with weak nitric acid. It dissolves, and the solution on evaporation deposits aurora red crystals of isatine, sparingly soluble in cold water, more soluble in hot water and in alcohol. By the action of chlorine, it yields two compounds in which hydrogen is partially replaced by chlorine. It may be volatilised if heated on a plate of metal. When acted on by a strong solution of potash, isatine is dissolved with an intense violet colour, which an addition of water and evaporation changes to yellow, and the liquid deposits pale yellow crystals, which contain potash, united to a new acid, isatinic acid, formed from isatine by the addition of 1 eq. water. When separated from its salts by stronger acids, isatinic acid is at once resolved into isatine and water; but if isatinate of lead be decomposed by sulphuretted hydrogen, and the filtered solution evaporated spontaneously in vacuo, the acid is obtained as a white flocculent powder, which when dissolved in boiling water, instantly becomes red, and the solution on cooling deposits crystals of isatine. Isatinic acid is $C_{16}H_6NO_5\,HO$. Its salts have the formula $C_{16}H_6NO_5, MO$. The violet-coloured compound first formed when isatine acts on potash is a compound of isatine and potash, which, when heated with water, soon passes into isatinate of potash.

With sulphurous acid, or rather sulphites, isatine forms salts of the formula $C_{16}H_5NO_4, 2SO_2 + MO$; which may be formed also by the action of sulphurous acid on isatinates.

By the action of chlorine, isatine is converted into two compounds, chlorisatine and bichlorisatine. When chlorine is passed through isatine or indigo suspended in water, both these compounds are formed, and they are separated by crystallisation, chlorisatine being the least soluble of the two.

Chlorisatine, $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right. NO_4$, forms transparent orange yellow 4-sided prisms, isomorphous with isatine, and very analogous to it in all respects. When acted on by potash, there is first formed a deep red solution, which when heated soon becomes yellow, and on cooling deposits brilliant pale yellow crystals of *chlorisatinate of potash*, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_5, KO$, a salt perfectly analogous to isatinate of potash, and containing an acid, chlorisatinic acid, which is chlorisatine, *plus* 1 eq. water, $C_{16}H_5ClNO_5$. Like isatinic acid, when separated from its salts it is speedily resolved into chlorisatine and water. *Chlorisatinate of silver,* $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5$, AgO forms yellow crystals, soluble in hot water. *Chlorisatinate of baryta,* $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5$, BaO, + 3 aq. forms golden yellow tables. *Chlorisatinate of lead,* $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5$, Pb O, when first precipitated from the salt of potash by nitrate of lead, forms a gelatinous yellow precipitate, which soon becomes flocculent, acquiring a splendid scarlet colour. The red salt is crystalline, the yellow amorphous. Chlorisatinate of copper forms at first a brownish yellow bulky precipitate, which soon changes to a heavy granular blood-red powder.

Like the isatinates, the chlorisatinates combine with the sulphurous acid, forming salts of the formula $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.NO_4, 2\,SO_2 + MO$. In short, the analogy between isatine and chlorisatine, isatinates and chlorisatinates, &c. is such as to furnish a very beautiful example of the substitution of chlorine for hydrogen, while the type or chemical character of the compound is unaffected. In bichlorisatine, we shall see an additional example of the same truth.

Bichlorisatine, $C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.NO_4$, is formed along with the preceding compound. It is more soluble than chlorisatine, but is otherwise remarkably similar to it. With aqua potassæ it first forms a deep red solution (here as in the case of isatine and chlorisatine a compound of it with potash), which when heated changes to yellow, and on evaporation yields yellow scales of a salt composed of potash and *bichlorisatinic acid.* The acid may be separated by stronger acids as a yellow powder, which when dissolved and warmed is resolved into bichlorisatine and water. Its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right.NO_5$, HO. The salt of *baryta,* $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right.NO_5$, BaO, forms golden yellow needles. The salt of *copper* is at first bulky and brown, but soon becomes greenish yellow and crystalline, and finally, a heavy granular powder of a fine carmine red colour.

Bichlorisatine with sulphites forms compounds analogous to those above mentioned of isatine and chlorisatine. In this case also, therefore, the type is perfectly retained, although 2 eq. of the hydrogen of isatine have been replaced by chlorine.

Bromine acts on isatine, and forms two compounds, *bromisa-*

tine and *bibromisatine,* entirely analogous to chlorisatine and bichlorisatine, forming *bromisatinic* and *bibromisatinic* acids, and also compounds with sulphites analogous to those just mentioned. We have, therefore, from isatine, and isatinic acid, by substitution, the following compounds:

Isatine	$C_{16}\ H_5\ NO_4$
Isatinic Acid . . .	$C_{16}\ H_6\ NO_5+HO$
Chlorisatine . . .	$C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.NO_4$
Chlorisatinic Acid . .	$C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_5+HO$
Bichlorisatine . . .	$C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.NO_4$
Bichlorisatinic Acid .	$C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right.NO_5+HO$
Bromisatine . . .	$C_{16}\left\{\begin{matrix}H_4\\Br\end{matrix}\right.NO_4$
Bromisatinic Acid . .	$C_{16}\left\{\begin{matrix}H_5\\Br\end{matrix}\right.NO_5+HO$
Bibromisatine . .	$C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right.NO_4$
Bibromisatinic Acid .	$C_{16}\left\{\begin{matrix}H_4\\Br_2\end{matrix}\right.NO_5+HO$
Isatinosulphites .	$C_{16}\ H_5\ NO_4, 2SO_2+MO$
Chlorisatinosulphites .	$C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right.NO_4, 2SO_2+MO$
Bichlorisatinosulphites .	$C_{16}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right.NO_4, 2SO_2+MO$
Bromisatinosulphites .	$C_{16}\left\{\begin{matrix}H_4\\Br\end{matrix}\right.NO_4, 2SO_2+MO$
Bibromisatinosulphites .	$C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right.NO_4, 2SO_2+MO$

Isatyde, $C_{16}H_6NO_4=C_{16}H_5NO_4,H$, is formed when an alcoholic solution of isatine is acted on by sulphuret of ammonium. It is a grey crystalline powder, and may be considered to represent isatine *plus* 1 eq. hydrogen.

Sulphésatyde, $C_{16}H_6N\left\{\begin{matrix}O_2\\S_2\end{matrix}\right.$ is isatyde, in which 2 eq. oxygen are replaced by sulphur. It is formed by the action of sulphuretted hydrogen on isatine dissolved in alcohol, and is a greyish yellow amorphous powder. *Sulphisatine* is the name of a compound obtained in the same way by Erdmann, which he considers to be different from sulphésatyde.

Chlorisatyde, $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right.NO_4$, is a white powder somewhat crystalline, obtained by the action of sulphuret of ammonium on chlorisatine. It is perfectly analogous to isatyde. By the action of sulphuretted hydrogen on chlorisatine, a compound is formed which is $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NS_4$; that is chlorisatyde, in which all the oxygen is replaced by the sulphur.

Bichlorisatyde, $C_{16}\left\{\begin{matrix}H_4\\Cl_2\end{matrix}\right. NO_4$ and *bibromisatyde*, $C_{16}\left\{\begin{matrix}H_4\\Br_2\end{matrix}\right. NO_4$, are perfectly analogous, in formation and properties, to chlorisatyde.

Sulphasatyde, $C_{16}H_6N\left\{\begin{matrix}O_3\\S\end{matrix}\right.$ is formed by the action of potash on sulphésatyde, from which it differs in having only 1 eq. oxygen replaced by sulphur. It is a white crystalline powder.

Indine, $C_{16}H_6NO_2$ is a crystallised substance, of a beautiful rose colour, formed by the action of potash on sulphesatyde, along with the preceding; or by the action of potash on sulphasatyde or isatyde. In the last case, isatinate of potash is also formed, thus, $3\ (C_{16}H_6NO_4) + 2\ KO = 2\ (KO,\ C_{16}H_6NO_5) + C_{16}H_6NO_2$. It is sulphésatyde, *minus* 2 eq. sulphur, and is also isomeric with white indigo. It is decomposed by nitric acid, and by bromine, which give rise to new products.

When indine, moistened with alcohol, is covered with a lukewarm solution of potash, it forms a black solution which in a few moments becomes a semisolid mass of black needles, which are a compound of potash with indine or rather with indinic acid, an acid formed from indine, like isatinic acid from isatine, by the assimilation of 1 eq. water, and which is very easily again resolved into indine and water.

Hydrindine is a yellow crystalline compound formed by heating indine, sulphasatyde, or isatyde with potash. Its composition is $C_{32}H_{13}N_2O_5$, that is 2 eq. indine *plus* 1 eq. water; and when strongly heated, it is resolved into indine and water. It is not composed of these substances, however, for it forms with potash a white salt, hydrindinate of potash. The acid in this salt appears to be formed, like some of those already described, by the addition of water to hydrindine; its formula is probably $C_{16}H_{15}N_2O_7,\ 2HO$.

Nitrindine, $C_{16}H_4N_2O_7$, is a beautiful violet-coloured powder formed by the action of nitric acid on indine and hydrindine. It is indine, in which 2 eq. hydrogen are replaced, one by oxygen, the other by nitrous acid; $C_{16}\left\{\begin{matrix}H_4\\NO_4\\O\end{matrix}\right\} NO_2$.

Chlorindine $C_{16}\left\{\begin{matrix}H_5\\Cl\end{matrix}\right. NO_2 + 2HO$, is a powder of a dirty violet colour, formed by the action of heat on chlorisatyde. Analogous compounds are obtained from *bichlorisatyde* and *bibromisatyde.* Bichlorindine is like chlorindine. Bibromindine is very dark red, and dissolves in alcohol with a fine purple colour.

The action of potash on isatyde appears to be the type of its action on chlorisatyde, bromisatyde, bichlorisatyde, and bibromisatyde. When isatyde is acted on by potash, it yields isatine (or isatinate of potash); indine (or indinate of potash); and hydrindine (or hydrindinate of potash). 6 eq. isatyde, ($6\,C_{16}\,H_6\,NO_4$) are equal to 4 eq. isatine ($4\,C_{16}\,H_5\,NO_4$) + 2 eq. indine ($2\,C_{16}\,H_6\,NO_2$) + 4 eq. water: or they are equal to 4 eq. isatine ($4\,C_{16}\,H_5\,NO_4$) + 1 eq. hydrindine ($C_{32}\,H_{13}\,N_2\,O_5$) + 3 eq. water. Both changes probably occur, and the three compounds, isatine, indine, and hydrindine, alike take up the elements of water to form the acids, which, to avoid confusion, are not here expressed. Now there is good reason to believe that precisely analogous changes occur when potash acts on bichlorisatyde and on bibromisatyde, each yielding three corresponding compounds and the three acids derived from these. The reader, by strictly following the analogy of the formulæ given above for the action of potash on isatyde, will easily be able to construct the equations for the other analogous cases.

When sulphesatyde is acted on by bisulphite of ammonia, there is formed among other products not fully investigated, a salt formed of ammonia united to a new acid, *sulphisatanous acid*, quite different from the acid in the salts formed when isatine is acted on by sulphites. This new acid is $C_{16}\,H_6\,NO_3$, $2\,SO_2 + HO$, or perhaps rather $C_{16}\,H_6\,N \left\{ \begin{matrix} O_2 \\ 2\,SO_2 \end{matrix} \right\} + HO$; that is, sulphesatyde, in which the 2 eq. of sulphur have been replaced by 2 eq. sulphurous acid.

The action of bisulphite of ammonia on sulphesatyde sometimes gives rise to the formation of different products: among others, to an insoluble white powder, *isatan*, $C_{16}\,H_6\,NO_3$, which when heated yields isatine and indine; $3\,(C_{16}\,H_6\,NO_3) = C_{16}\,H_5\,NO_4 + 2\,(C_{16}\,H_6\,NO_2) + HO$. Both indine and nitrindine, when acted on by bisulphite of ammonia, appear to produce compounds analogous to those derived from sulphesatyde.

Chlorindopten is the name given by Erdmann to a volatile crystalline substance, formed along with chlorisatine and bichlorisatine, when chlorine acts on indigo. When the chlorinised mass is distilled with water, this substance passes over in white crystals, which are acid, and evidently a mixture of two substances. When this chlorindopten is heated with potash, a neutral substance passes over, in white crystals similar to the original ones; this is *chlorindatmit;* while the potash retains an acid of a disagreeable odour, *chlorindoptenic acid.*

Chlorindoptenic acid, $C_{12}H_4Cl_3O, HO$, is separated from its potash salt by acids, as a white flocculent matter of a very disagreeable odour. Laurent has identified it with his chlorophenisic acid, an acid derived from coal tar by the action of chlorine, and makes its formula $C_{12}\left\{\begin{matrix} H_2 \\ Cl_3 \end{matrix}\right\} O, HO$. Chlorindatmit appears to be $C_{12}\left\{\begin{matrix} H_4 \\ Cl_3 \end{matrix}\right\} N$ (Hofmann).

By the further action of chlorine on chlorisatine or bichlorisatine, dissolved in alcohol, new compounds are formed, among which are, *chlorinised chlorindopten,* which, like chlorindopten, is a mixture apparently of chlorindatmit, with an acid, *chlorinised chlorindoptenic acid,* $C_{12}Cl_5O, HO$; which is the *chlorophenusic acid* of Laurent. This acid is accompanied by *chloranile,* $C_{12}Cl_4O_4$, a neutral body in volatile golden yellow scales, soluble in hot alcohol, which is also derived from the oil of coal tar, or rather from the hydrate of phenyle or carbolic acid of that oil, from which chlorophenisic and chlorophenusic acids are obtained.

Chloranile dissolves in weak potash with a deep purple colour, and the solution deposits dark, purplish-red crystals, composed of potash and a new acid, *chloranilic acid.* This acid forms scarlet or yellow crystals, according as it contains water of crystallisation or not. Its formula is $C_{12}Cl_2O_6, 2HO$, or C_6ClO_3, HO.

When chloranile is acted on by aqua ammoniæ, it is dissolved, forming a blood-red solution, which deposits chesnut-brown crystals of *chloranilammon* $C_6H_3NClO_3 + 4aq = C_6ClO_3 + NH_3 + 4aq$. It dissolves in water with a purple colour, and when a saturated solution is mixed with hydrochloric acid, it deposits very brilliant black needles of great length. These are a new compound, *chloranilam,* $C_{12}Cl_2H_3NO_6 = C_{12}Cl_2O_6 + NH_3$; that is 2 eq. of chloranilammon, $2(C_6ClO_3, NH_3) = C_{12}Cl_2O_6, N_2H_6$; minus 1 eq. ammonia NH_3. Both these compounds give precipitates with metallic solutions, which are the same from both, but distinct from those formed by chloranilic acid or its salts. Chloranilammon, according to Laurent, is the ammonia salt of an acid containing amide as an ingredient. Chloranilam is the acid itself.

By the action of ammonia on isatine there are produced several new compounds, varying with the strength of the ammonia, and the menstruum employed. In these compounds, oxygen is replaced by *amide,* NH_2, or *imide,* $\frac{1}{2}NH = Im$.

Imasatine is formed when dry ammonia is passed through an alcoholic solution of isatine. It forms fine deep yellow crystals, the formula of which is $C_{16}H_6N_2O_2 = C_{16}H_5N\left\{\begin{matrix}O_2\\2\,Im.\end{matrix}\right.$

Imasatine is formed when aqua ammoniæ acts on a solution of isatine in alcohol. It is a greyish yellow crystalline substance, the formula of which is $C_{16}H_5N\left\{\begin{matrix}O_3\\Im\end{matrix}\right.$?

Imasatinic acid is formed along with the preceding, and is dissolved along with ammonia. By the addition of an acid it is precipitated as a beautiful scarlet crystalline powder, soluble in hot alcohol, which deposits it in splendid tabular crystals similar to the sublimed periodide of mercury. It dissolves sparingly in acids with a violet colour, and these solutions deposit violet crystals. Its formula is $C_{16}H_5N\left\{\begin{matrix}O_3\\Im\end{matrix}\right\} + HO.$

Amasatine is formed along with the two preceding bodies. It has a fine yellow colour, and dissolves in acids with a violet colour, apparently passing into imasatinic acid. Its formula is $C_{16}H_5N\left\{\begin{matrix}O_3\\Ad\end{matrix}\right\} + HO.$ (Ad$=NH_2=$amide.)

The analogy between chlorisatine, &c. and isatine, holds in regard to the action of ammonia on them. By the action of dry ammonia on an alcoholic solution of chlorisatine there is formed a yellow crystalline compound, analogous to imesatine. It is called *Imechlorisatinase,* and its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}N\left\{\begin{matrix}O_2\\2\,HN.\end{matrix}\right.$

Imachlorisatinase is analogous to imasatine. Its formula is $C_{16}\left\{\begin{matrix}H_4\\Cl\end{matrix}\right\}N\left\{\begin{matrix}O_3\\NH.\end{matrix}\right.$ It forms brownish yellow crystals.

Imabromisatinese, formed by the action of dry ammonia on bibromisatine in alcohol, is $C_{16}\left\{\begin{matrix}H_3\\Br_2\end{matrix}\right\}N\left\{\begin{matrix}O_3\\NH.\end{matrix}\right.$ It is a deep orange crystalline powder.

We have now briefly run over the catalogue of the very remarkable compounds derived from indigo by the action of sulphuric acid and bichromate of potash, which produces isatine, and by the action of chlorine either on indigo or on isatine, of bromine on the same, and of potash, ammonia, sulphuretted hydrogen and sulphuret of ammonium on the products of these actions. The nomenclature of these compounds is in a very imperfect state, and requires reformation, but this cannot be effected until the substances themselves have been more thoroughly studied. It is most important to observe, that by or through chloranile and the chlorindoptenic acids, the series to which indigo belongs connects itself with that of carbolic acid or hydrate of phenyle (to be afterwards described), and these again with the series of salicyle. We have now to mention one or two products of the action of nitric acid on indigo which are common to all these series, and like chloranile, seem likely to be very frequently met with as products of the decomposition of organic compounds.

Anilic acid, Syn. *Indigotic acid*, *Nitrosalicylic acid*, $C_{14}\,H_4\,NO_9$, HO. This acid is formed by the long-continued action of weak nitric acid on indigo. It is also formed in the preparation of isatine, if the action be pushed too far. It is identical with nitrosalicylic acid, obtained by the action of nitric acid on salicylic acid or on salicine. It forms fine yellowish-white prisms, which are light and bulky, and shrink much in drying. It is fusible and volatile. By the action of strong nitric acid it is converted into oxalic and picric acids. It requires 1000 parts of cold water for solution. Its salts crystallise well, and their general formula is $C_{14}\,H_4\,NO_9$, MO. The anilate of oxide of methyle is obtained as a crystalline compound by the moderated action of nitric acid on the salicylate of oxide of methyle (oil of gaultheria). The anilate of oxide of ethyle is exactly similar.

Picric acid, Syn. *Carbazotic acid*, *Nitropicric acid*, *Nitrophenisic acid*, $C_{12}\left\{\begin{matrix} H_2 \\ 3\,NO_4 \end{matrix}\right\}O,\ HO$. This acid is formed by the action of nitric acid on anilic acid, indigo, salicine, salicylic acid, hydrate of phenyle or carbolic acid, coumarine, silk, aloes (?) and other substances. It is most easily formed from carbolic acid, salicine or oil of gaultheria, by the action of an excess of fuming nitric acid assisted by heat. It is purified by solution in hot water and recrystallisation. It forms pale yellow or even white scales of a silvery lustre. They dissolve in hot water with a strong yellow colour, and a very bitter taste. The acid is fusible and volatile. Its salts crystallise most readily, and all explode when heated. When these salts are put in contact with lime and green vitriol, blood-red solutions are formed, containing the lime salt of a new acid. The picrate of potash is so sparingly soluble, especially in alcohol, that an alcoholic solution of picric acid may be used as a test for potash.

Picric acid is interesting as occurring among the products of the decomposition by nitric acid of so many different substances. It is easily derived from the series of phenyle, that is, from carbolic acid, $C_{12}\,H_5\,O$, HO. Derived from this, we have Chlorophenesic acid, $C_{12}\left\{\begin{matrix} H_3 \\ Cl_2 \end{matrix}\right\}O,\ H\,O$, Chlorophenusic acid, $C\ _{2}\,Cl_5\,O,\ H\,O$, and Picric acid, $C_{12}\left\{\begin{matrix} H_2 \\ 3\,NO_4 \end{matrix}\right\}O,\ HO$.

It is, therefore, carbolic acid in which 3 eq. of hydrogen are replaced by 3 eq. of nitrous acid.

When indigo is heated with concentrated potash, there are formed two new acids: *chrysanilic acid*, the composition of which is uncertain, and *anthranilic acid*, $C_{14}H_7NO_4 = C_{14}H_6NO_3, HO$. The latter is purified in the form of anthranilate of potash, and the acid separated by an excess of acetic acid. It forms transparent yellow scales, which, however, when quite pure, are colourless. It is derived from blue indigo, $C_{16}H_5NO_2$, by the loss of 2 eq. carbon and the addition of 2 eq. water.

When anthranilic acid is mixed with powdered glass, and rapidly heated, it is resolved into carbonic acid and an oily liquid, which is *aniline*, a very powerful base, devoid of oxygen, identical with the *crystalline* of Unverdorben, and the *kyanol* of Runge, $C_{12}H_7N$. This metamorphosis is very simple: $C_{14}H_7NO_4 = C_2O_4 + C_{12}H_7N$. Since aniline is obtained in many other cases of decomposition of organic matters by heat, it becomes a substance of great interest.

Aniline is recognised by its property of striking a deep violet blue colour with chloride of lime. It obtained the name *kyanol* from this property. Its other name, *crystalline*, indicates its great tendency to form crystallisable salts with acids.

The recent researches of A. W. Hofmann have greatly extended our knowledge of this remarkable compound. He has shown that it is not confined to the products of the decomposition of indigo, but that it is formed when other substances, isomeric with anthranilic acid, are exposed to heat along with bases, such as lime or baryta. Such substances are salicylamide and protonitrobenzoéne, both of which have the empirical formula $C_{14}H_7NO_4$. The former yields little, but the latter is entirely resolved into aniline and carbonic acid. He has also fully identified aniline with the *crystalline* of Unverdorben, a base occurring with others among the products of distillation of animal matter, and in coal tar. It is worthy of remark that a close connection may be traced between aniline and carbolic acid (hydrate of phenyle). The latter is $C_{12}H_5O, HO$. The carbolate of ammonia, $C_{12}H_5O, NH_4O$, minus 2 eq. water would yield an amide, *phenylamide*, which would be $C_{12}H_5, NH_2 = C_{12}H_7N$; and this is aniline. Now in Hofmann's experiment above mentioned, in which salicylamide was heated with lime, it did not yield much aniline, but, on the other hand, it furnished a large quantity of carbolic acid.

It is further to be noticed that carbolic acid (hydrate of phenyle) and aniline (phenylamide) occur together in coal tar;

and that all the substances which yield either one or other of these are also converted into picric acid, $C_{12}\left\{\begin{matrix}H_2\\3NO_4\end{matrix}\right\}O, HO$, by the action of nitric acid. Thus carbolic acid, indigo, salicine, and salicylic acid, are all transformed into picric acid by excess of nitric acid.

Another point in which all these substances agree is this, that when acted on by a mixture of hydrochloric acid and chlorate of potash, they are all converted into chloranile, $C_{12}Cl_4O_4$. It is more than probable that all those bodies, such as indigo, salicine, carbolic acid, &c. which in this way yield chloranile, either belong to the series of phenyle or are nearly allied to that series, and readily pass into it. The fundamental or primitive compound of that series appears to be some compound of the formula $C_{12}\Delta_8$, where Δ stands for hydrogen, chlorine, bromine, iodine, oxygen, nitrous acid, &c. &c. Assuming this, and supposing Δ to be represented by H, then we have the following series, which will exhibit in a practical form the doctrine of substitutions.

$$C_{12}\ H_8 = \text{Supposed origin or nucleus of the series.}$$

$$C_{12}\left\{\begin{matrix}H_6\\O_2\end{matrix}\right\} = C_{12}\ H_5\ O, HO = \text{hydrate of phenyle.}$$

$$C_{12}\left\{\begin{matrix}H_4\\Cl_2\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}O, HO = \text{chlorophenesic acid.}$$

$$C_{12}\left\{\begin{matrix}H_3\\Cl_3\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O, HO = \text{chlorophenisic acid.}$$

$$C_{12}\left\{\begin{matrix}H\\Cl_5\\O_2\end{matrix}\right\} = C_{12}\,Cl_5, O, HO = \text{chlorophenusic acid.}$$

$$C_{12}\left\{\begin{matrix}Cl_4\\O_4\end{matrix}\right\} = \text{chloranile.}$$

$$C_{12}\left\{\begin{matrix}H_7\\N\end{matrix}\right\} = \text{aniline.}$$

$$C_{12}\left\{\begin{matrix}H_4\\2\,NO_4\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_3\\2\,NO_4\end{matrix}\right\}O, HO = \text{nitrophenesic acid.}$$

$$C_{12}\left\{\begin{matrix}H_3\\3\,NO_4\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_2\\3\,NO_4\end{matrix}\right\}O, HO = \text{nitrophenisic (picric) acid.}$$

$$C_{12}\left\{\begin{matrix}H_3\\Br_3\\O_2\end{matrix}\right\} = C_{12}\left\{\begin{matrix}H_2\\Br_3\end{matrix}\right\}O, HO = \text{bromophenisic acid.}$$

Hofmann has shown that isatine, when distilled with potash, yields aniline ; and that chlorisatine, so analogous in all respects to isatine, undergoes a similar decomposition, yielding a new base, *chloraniline ;* also that other compounds may be formed containing more chlorine, but still belonging to the same series ; finally, that bromisatine also yields a base, bromaniline. The following are the formulæ of these new compounds, which, it will be observed, are still referable to the original formula, $C_{12}\Delta_8$ or $C_{12}H_8$.

$C_{12}\left\{\begin{matrix}H_6\\Cl\\N\end{matrix}\right\}$ = chloraniline, a powerful base.

$C_{12}\left\{\begin{matrix}H_5\\Cl_2\\N\end{matrix}\right\}$ = dichloraniline, a weak base.

$C_{12}\left\{\begin{matrix}H_4\\Cl_3\\N\end{matrix}\right\}$ = trichloraniline = chlorindatmit of Erdmann, a neutral body.

$C_{12}\left\{\begin{matrix}H_6\\Br\\N\end{matrix}\right\}$ = bromaniline, a base.

$C_{12}\left\{\begin{matrix}H_5\\Br_2\\N\end{matrix}\right\}$ = dibromaniline, a weak base.

$C_{12}\left\{\begin{matrix}H_4\\Br_3\\N\end{matrix}\right\}$ = tribromaniline = bromaniloid of Fritzsche, a neutral compound.

It may here be mentioned, that although, in order to include the water of the hydrated acids, I have adopted $C_{12}H_8$ as the nucleus of these compounds, we may also refer them to $C_{12}H_6$ =phène or benzine. The oxide of phenyle and the different acids will then be represented as anhydrous, thus, $C_{12}\left\{\begin{matrix}H_5\\O\end{matrix}\right.$ oxide of phenyle, &c. Aniline will be $C_{12}\left\{\begin{matrix}H_5\\NH_2\end{matrix}\right. = C_{12}\left\{\begin{matrix}H_5\\Ad\end{matrix}\right.$ = phenylamide ; and chloraniline will be $C_{12}\left\{\begin{matrix}H_4\\Cl\\Ad\end{matrix}\right.$; and so on. The only compound which does not adapt itself to this formula is chloranile, $C_{12}Cl_4O_4$; which might, however, be $C_{12}\left\{\begin{matrix}Cl_3\\O_2\\ClO_2\end{matrix}\right.$, or $C_{12}\left\{\begin{matrix}Cl_2\\O_2\\2ClO\end{matrix}\right.$.

Our space will not permit us to enter into any details concerning the preparation and properties of these interesting compounds; but it may be remarked that chloraniline by the action of hydrochloric acid and chlorate of potash yields chloranile; and that the same substance, when passed over lime (hydrated ?) at a low red heat, yields aniline, thus affording additional proof that all these compounds belong to one series, and are different subtypes of one general type. Nor must it be forgotten, that in the case of aniline, chloraniline, and bromaniline, we have chlorine and bromine substituted for hydrogen in a basic compound, without affecting its basic characters. This is the first known example of a base formed by substitution from another base, although similar facts, in regard to acids and neutral bodies, had long been known.

10. Carmine.

This name has been given to the colouring matter of cochineal which is nitrogenised, and may be obtained in dark red crystalline grains, very soluble in water and alcohol. It forms with alumina a beautiful red lake, well known as carmine. Its precise formula is not determined, but it approaches to $C_{32} H_{24} N O_{20}$.

ACTION OF NITRIC ACID ON ALOES.

This action so much resembles, in some points, the action of nitric acid on indigo, that it may be properly mentioned here. Aloes is the well-known inspissated juice of certain species of *aloe*, and is very bitter and purgative. The nature of its active principle is still unknown: but when heated with nitric acid it yields a yellow bitter substance, which is converted, by the further action of the acid, into two crystallisable acids, chrysammic and chrysolepic acid. The artificial bitter of aloes appears to be formed of two acids, aloetic and aloeretinic acids, which form red salts, but the composition of which is not exactly ascertained.

Chrysammic acid, $C_{15} H N_2 O_{12}, HO$, is obtained as a yellow precipitate, when water is added to the solution obtained by heating aloes with excess of nitric acid. It is purified by being combined with potash, and this salt, after recrystallisation, is dissolved in hot water and decomposed by diluted nitric acid. The chrysammic acid is deposited as a powder formed of golden yellow shining scales. Its solution is of a fine purple. All its salts are crystallisable and of a deep red colour, frequently with green reflection, like muroxide. The chrysammate of ammonia forms dark green crystals, which, when dissolved and acted on by nitric acid, deposit brilliant black scales, which are not chrysammic acid, but are transformed into it when boiled with acids or bases. The solution of chrysammate of ammonia gives with metallic salts peculiar precipitates distinct from those formed with the same salts by chrysammate of potash.

Chrysolepic acid, $C_{12} H_2 N_3 O_{13}, HO$, has the formula and many of the properties of picric acid; but is said by Schunk, who, discovered it, to be different. It is darker in colour, and its salt with potash is much more soluble than picrate of potash. It would, however, appear that the two acids are essentially the same; for their salts are in general very similar, and all explode when heated. Now that picric acid is recognised as so frequent a product of the action of nitric acid, we have no difficulty in understanding its occurrence here.

ALKALOIDS OR ORGANIC BASES.

These names are given to a class of nitrogenised organic compounds which, in their relations, are quite analogous to ammonia, or rather to oxide of ammonium. They are to be distinguished from such basic oxides as oxide of ethyle, oxide of methyle, &c., which contain no nitrogen, and, although they form neutral compounds with acids, yet exist in a peculiar state in these compounds, which cannot be decomposed, like ordinary salts, by double decomposition. Thus oxalate of oxide of ethyle does not precipitate with nitrate of lime, and chloride of ethyle does not decompose nitrate of silver. But the case is quite different with the alkaloids; for their salts undergo the same decompositions as those of ammonia.

Most of the alkaloids are found in vegetable juices, seeds, or roots; these are called vegetable alkalies, and they are generally the active principles of the plants, for the most part poisonous, in which they are found. But of late organic bases quite analogous to those produced by nature, have been formed in a variety of processes; as, for example, the singular bases containing platinum, described at pp. 269-271; the bases containing arsenic, or arsenic and platinum, mentioned at pp. 382-384; the bases of coal tar, of which aniline, formed in several different processes, is one; the bases, chloraniline, &c., derived from aniline; the bases derived from oil of mustard, (see p. 449); those derived from the decomposition of natural alkaloids, as *quinoleine* and *cotarnine;* and, finally, those formed by the action of sulphuret of ammonium on certain nitrogenised bodies, as aniline from nitrobenzide, naphthalidine from nitronaphthalese, &c. Most of these artificially formed bases are of very recent discovery, and it is evident that they must throw much light on the theory of the production of the natural alkaloids, and that the careful study of this part of the subject will, in all probability, eventually lead to the artificial formation of the natural organic bases.

The alkaloids possess, for the most part, very decided basic properties; when dissolved they act on vegetable colours like the inorganic alkalies; and they neutralise the strongest acids completely, generally forming crystallisable salts. Most of them, at the ordinary temperature, are expelled from their salts by ammonia, but many of them at the heat of boiling water expel ammonia from its salts, owing to the volatility of the latter alkali.

Their basic properties are not derived from the oxygen they contain, for no variation in the amount of that element affects their neutralising power. On the other hand, there is every reason to believe that their basic character depends on the nitrogen they contain; for they all, without exception, contain nitrogen, although several are devoid of oxygen. Moreover, most, if not all of those which have been formed artificially, are prepared with the aid of ammonia, or some compound of ammonia, or amidogen. It is quite conceivable that they may be composed of ammonia or amidogen, *plus* some compound of carbon and hydrogen, or of carbon, hydrogen, and oxygen, the addition of which does not diminish the basic energy of the ammonia, or amidogen. Thus, the three bases containing platinum, formerly described, may be represented as PtO, NH_3, $PtO, 2NH_3$, and $PtClO, 2NH_3$; and these formulæ will at all events show their relation to ammonia.

The alkaloids occur in combination, generally with vegetable acids; and they are separated from these combinations by the same means which are employed in the case of inorganic bases, modified in each case, according as the alkaloid is soluble or insoluble in water and other solvents, fixed or volatile when heated. Thus quinine, morphia and strychnia, are separated by adding to their soluble salts, lime, ammonia, or magnesia, which form soluble salts with the acids which are present, while the alkaloids, being insoluble, are precipitated; codeine, being soluble in ether as well as water, is first set free by potash, and ether being added to the aqueous liquid, is agitated with it, and rises to the surface, carrying the codeine along with it, and the same process applies to other alkaloids. Lastly, conia, nicotine, and other volatile alkaloids are obtained by distilling their salts with an excess of liquor potassæ.

The alkaloids, like ammonia, combine with hydrogen acids forming salts, without the addition of water or its elements being necessary; they also, like ammonia, refuse to combine with anhydrous oxygen acids, requiring 1 eq. of water to form dry salts. Their hydrochlorates, like sal ammoniac, form double salts with the bichlorides of platinum and of mercury.

The salts of most of the alkaloids are precipitated as tannates by infusion of galls.

The alkaloids are generally decomposed by chlorine, bromine, and iodine, forming coloured compounds not yet fully investigated. They are also decomposed by nitric acid, some of them with a deep red colour.

Some of them, such as quinine, strychnia, &c. when heated with strong caustic potash, yield an oily compound, which is also a base, and is called quinoleine.

We shall now briefly describe the individual alkaloids, dividing them into groups, according to their characters.

1. Liquid Volatile Bases.

a. Aniline, $C_{12} H_7 N$, has been already mentioned as formed by the action of potash on isatine, and by the action of heat and bases on anthranilic acid and protonitrobenzoene, and on salicylamide, although the latter only yields a very small proportion. It also occurs as one of the most remarkable ingredients in the oil of coal-tar, where it is associated with two other bases, leukol and pyrrol; also in the oil obtained by distilling indigo, or animal matter. In coal-tar it is associated or combined with carbolic acid, and the relation between aniline (phenylamide) and carbolic acid (hydrate of phenyle) has already been explained. It is obtained pure by rather a tedious process.

Aniline is an oily liquid, boiling at 358°, rather heavier than water (Sp. G. 1·028), of a very high dispersive and refractive power. It has a hot pungent taste, and an agreeable vinous odour. It forms crystalline salts with most acids, and strikes a deep violet-blue colour with solution of bleaching-powder. By the action of nitric acid it is converted into picric acid, and by that of a mixture of hydrochloric acid, and chlorate of potash, it is converted into chloranile. Chromic acid causes a deep bluish-black colour. With chlorine it yields chlorinised compounds, especially chlorophenisic (chlorindoptenic) acid, and trichloraniline (chlorindatmit). Bromine converts it into tribromaniline (bromaniloide). Aniline is very acrid and poisonous. The two bases, chloraniline, $C_2 H_6 Cl N$, and bromaniline, $C_{12} H_6 B_2 N$, derived from aniline by substitution, have been already mentioned. They are very analogous to aniline.

b. Leukol, $C_{18} H_8 N$. This base is found in the oil of coal-tar, along with aniline, from which it is separated by distillation, aniline being the more volatile of the two. Leukol is an oily liquid, of a still higher refractive and dispersive power than aniline; it has an unpleasant smell, and a burning taste. It boils at 463°. Its Sp. G. is 1·081. Neither bleaching-liquor nor chromic acid produce, with leukol, the blue colour which they give rise to with aniline. It combines with acids, but its salts do not crystallise so readily as those of aniline.

c. Nicotine, $C_{10} H_8 N$. This base is found in tobacco, and is obtained by distilling the concentrated infusion of the leaves along with potash. The distilled liquid, which contains nicotine, water, and ammonia, is neutralised by sulphuric acid and the neutral solution dried up. Alcohol then dissolves the sulphate of nicotine, leaving undissolved the sulphate of ammonia. The pure sulphate, distilled with potash, yields pure nicotine, which appears as an oily, limpid, colourless liquid, having a weak smell of tobacco. Its Sp. G. is 1·048. It is decidedly alkaline, and mixes with water, alcohol, and ether. It is highly poisonous. With acids it forms salts which crystallise with difficulty. The hydrochlorate of nicotine combines with bichloride of platinum, forming a double salt, which yields large regular orange-red crystals, of the formula $C_{10} H_8 N, H Cl + Pt Cl_2$. It is probable that nicotine, besides being found in the fresh leaves of tobacco, is produced in larger quantity during the fermentation to which the leaves are subjected in the manufacture of tobacco; and there is also reason to believe that it is produced by the action of heat on tobacco, as in smoking, and that, from the comparative simplicity of its formula, it will be found among the products of the distillation of organic compounds containing nitrogen. Its analogy, in composition and properties, to the two preceding bases, is very obvious.

d. Conine. Syn. *Conia.* $C_{16} H_{16} N$? This base occurs in the hemlock, *conium maculatum*, and is extracted by a process quite analogous to that above described for nicotine. It is also an oily liquid, boiling at 338°, highly poisonous, and easily decomposed. Its taste and smell are both very acrid and disagreeable, and somewhat analogous to those of nicotine. Its salts are acrid and poisonous, crystallising with difficulty. As it is the active principle of the conium, conine, either pure or as a salt, ought to be used instead of the extract or tincture, which are very variable.

e. Quinoline, $C_{19} H_8 N$. This base is formed artificially, by distilling quinine, cinchonine, or strychnine, along with caustic potash. It is an oily liquid, of Sp. G. 1·084, which is volatile at a high temperature. It forms two hydrates, with 1 and 3 eq. of water respectively. It is very bitter, and strongly alkaline, and forms crystallisable salts with acids. Its production from quinine and cinchonine will be explained under these bases. Quinoleine is now believed to be identical with leukol.

2. Bases derived from Oil of Mustard.

Under the head of Oil of Mustard, these bases have been already described. They are *Thiosinnamine*, $C_8 H_4 NS_2$; *Sinnamine*, $C_8 H_3 N$; and *Sinapoline*, $C_{14} H_6 NO_2$.

3. Bases of Cinchona Bark.

a. Quinine, $C_{20} H_{12} NO_2$. This important alkaloid is found along with cinchonine, in most species of cinchona bark. It predominates in yellow bark, *Cinchona flava*, *China regia*, or *C. calisaya;* and is obtained by boiling with an excess of milk of lime the decoction in diluted hydrochloric acid of the bark, and treating the precipitate with hot alcohol, which dissolves cinchonine and quinine. On evaporation, the cinchonine is deposited in crystals, and the quinine remains dissolved. Water is added, which causes the quinine to separate as a resinous mass. It may be obtained in crystals by the spontaneous evaporation of its solution in absolute alcohol. It is very sparingly soluble in water, but very soluble in alcohol and in acids. Its solutions are very bitter. When heated with hydrate of potash, it yields carbonate of potash, hydrogen gas, and quinoline. $C_{20} H_{12} NO_2 + KO = KO, CO_2 + C_{19} H_8 N + H_4$.

Quinine is decidedly alkaline, and neutralises the acids. Its salts, especially the sulphate, are very much used in medicine, especially as febrifuge and tonic remedies, in most cases very superior to the bark in substance. The sulphate of quinine used in medicine is a basic salt, $2(C_{20} H_{12} NO_2) + SO_3 + 8HO$. The neutral sulphate is much more soluble in water; hence, in draughts, sulphate of quinine is generally dissolved in diluted sulphuric acid. The hydrochlorate, phosphate, citrate, and ferrocyanate of quinine have also been employed in medicine.

b. Cinchonine, $C_{20} H_{12} NO$. This base predominates in the grey bark, *Cinchona condaminea*, or *C. rubiginosa*, and is also found in large quantity, as well as quinine, in red bark, *C. oblongifolia*. Its preparation has been above described. It crystallises very readily, and is not so bitter as quinine, although highly febrifuge. When heated, a considerable part is sublimed. When distilled with potash, it yields quinoline. $C_{22} H_{12} NO + HO, KO = KO, CO_2 + C_{19} H_8 N + H_5$. It neutralises the acids, forming crystallisable salts, which may be substituted for those of quinine.

It is very important to observe that cinchonine only differs from quinine by 1 eq. oxygen; and although hitherto no one has succeeded in converting one into the other, little doubt can be entertained that this will be accomplished in process of time. The fact that both yield quinoline is very interesting.

c. Quinoidine. This name has been given by Sertuerner to a third alkaloid, which he has found in the mother liquors of the preceding. It would appear to possess a very great neutralising power, but is not yet known in a state of purity. The subject requires investigation.

d. Aricine, $C_{20}H_{12}NO_3$. This base was found, in 1828, in a cinchona bark from Arica, in Peru, and has not since occurred. It is very similar to cinchonine, from which it differs in being soluble in ether. According to the analysis of Pelletier, it contains 1 eq. oxygen more than quinine, and 2 eq. more than cinchonine, so that the three bases may be viewed as oxides of the same radical. Aricine forms salts which are crystallisable, bitter and febrifuge.

Besides the above four, other alkaloids are said to have been found in different species of cinchona; as *pitoyine*, in the *China pitoya*, *chinovine* in the *China nova*, another alkaloid in the *China of Carthagena*, *blanquinine* in the *China blanca*, which is the bark of *cinchona ovifolia* and *C. macrocarpa;* and *cinchovatine* in *Cinchona ovata*. This last crystallises well, and forms crystallisable salts. It has been analysed, and the results lead to the formula $C_{46}H_{27}N_2O_8$.

4. Bases of the Papaveraceæ.

a. Morphine. $C_{35}H_{20}NO_6$. This alkaloid occurs in opium, which is the inspissated juice of *papaver somniferum*. Perhaps the easiest method of extracting it is the following. The soluble part of opium is extracted by water, and the concentrated infusion is mixed with solution of chloride of calcium, this salt being added in slight excess. On standing, especially if warmed, the mixture deposits a copious brownish grey precipitate of mixed meconate and sulphate of lime (the morphia being in the opium partly as meconate, partly as sulphate), while hydrochlorate of morphia remains in solution with a very large proportion of dark brown colouring matter. The brown solution is evaporated till, on cooling, the hydrochlorate crystallises, forming a nearly solid mass, which is subjected to very strong pressure in flannel. A thick, viscid, nearly black mother liquor is thus expressed, which contains all the narcotine and colouring matter. The squeezed mass or cake of hydrochlorate of morphia is of a fawn colour. It is redissolved in hot water, filtered if necessary, and recrystallised, so much water being used, that on cooling a semisolid mass is obtained. This is again squeezed out, and if the squeezed cake is not quite white, it is only necessary to repeat the operation. A little animal charcoal, in the second, or better still in the third, crystallisation, assists in removing the last traces of colour. The second and third mother liquids, although coloured, are not to be thrown away, but should be added to the solution of a fresh portion of opium, so that the small quantity of hydrochlorate which is retained in solution shall not be lost. In crystallising hydrochlorate of morphine, the liquid should always be acidulated with hydrochloric acid (after the animal charcoal is separated), because in this way very little indeed is retained in solution.

The purified hydrochlorate, which still contains about $\frac{1}{30}$ of codeine, is now dissolved in hot water, and supersaturated with ammonia ; on cooling, the morphine is deposited as a snow-white crystalline powder, which may be crystallised by means of hot alcohol. The codeine remains in the mother liquor.

Morphine forms hard transparent brilliant crystals, almost insoluble in water, soluble in hot alcohol, insoluble in ether. It is decidedly alkaline, neutralising acids, and forming crystallisable salts. All its solutions are bitter, and act as narcotic poisons. It is coloured red by nitric acid, and brownish-red by iodic acid ; it also strikes a deep blue with perchloride of iron.

The salts of morphine are much used in medicine, especially the hydrochlorate, the acetate, and the sulphate. A solution of any of these salts, of five grains to the ounce, may be administered in the same dose as tincture of opium (laudanum). The hydrochlorate or muriate is prepared as above described, and is used in the state in which it is obtained by repeated crystallisation, containing $\frac{1}{15}$ of its weight of a double hydrochlorate of morphia and codeine, which has much the same action. The acetate and sulphate are best made directly by dissolving in acetic and sulphuric acids the precipitated morphine till they are neutralised, and then evaporating. 1 lb. of good opium yields $1\frac{1}{2}$ oz. of hydrochlorate of morphine. These salts are most valuable anodynes, and do not derange the stomach nearly so much as an equivalent dose of laudanum ; but they do not act so decidedly in producing sleep as in allaying pain and irritation ; at least the sleep they induce does not come on so soon as in the case of laudanum. The patient, however, even when he does not sleep, feels refreshed, almost as if he had slept, and on the whole the preparations of morphine are preferred by the physician, and have, in this country at least, nearly banished the use of laudanum. The black drop contains impure citrate of morphine.

b. Codeine. $C_{35}H_{20}NO_5$. This alkaloid is obtained as above described, from the mother liquor of the precipitated morphine, which, being evaporated, deposits the double hydrochlorate of morphine and codeine. This salt being purified, is acted on by potash, which dissolves the morphine, while the codeine is left as a viscid mass, which soon becomes hard and crystalline. It is purified by solution in ether or in water, both of which solvents leave the morphine, which may be mixed with it, undissolved. The ethereal solution, by spontaneous evaporation, deposits it, especially if a little water be added, in fine anhydrous prisms; the aqueous solution gives large octahedral crystals, which are a hydrate, with 2 eq. of water.

Codeine is a powerful base, forming neutral salts with acids. Its solutions are bitter, and would seem to have an anodyne action on the system. But in certain circumstances they appear to excite intolerable itching of the whole skin. It is therefore possible, that the itching caused in some persons by opium, and by the commercial muriate of morphine, proceeds from codeine.

It is important to observe that, as cinchona bark contains three alkaloids differing only in the proportion of oxygen they contain, so the two principal bases of opium differ only by 1 eq. oxygen. Hitherto, however, it has been found impossible to convert codeine into morphine by oxidation, or morphine into codeine by deoxidation.

c. Thebaine. This base also occurs in opium. It is nearly insoluble in water, soluble in alcohol and ether. Its solutions are alkaline, and have an acrid metallic taste. It forms crystallisable salts with acids. According to Kane, its formula is $C_{25}H_{14}NO_3$.

d. Pseudomorphine, $C_{27}H_{18}NO_{14}$? This base is occasionally found in opium. It forms shining scales. It is sparingly soluble in water and weak alcohol, insoluble in absolute alcohol and in ether. It is readily dissolved by caustic potash or soda. It is coloured blue by perchloride of iron. It forms salts with acids, which are as yet little known.

e. Narceine, $C_{28}H_{20}NO_{12}$? This, which is a feeble base, also occurs in opium. It is sparingly soluble in water, soluble in alcohol, insoluble in ether. It melts at 197°. It is coloured blue by hydrochloric acid, but not by perchloride of iron. Acids dissolve it, but hardly form definite salts with it. In short, it ought rather to be described as an indifferent substance, were it not that its composition so much resembles that of the alkaloids.

f. Narcotine, $C_{46}H_{25}NO_{14}$. This is another weak base, found in opium in larger proportion than any other, except morphine. It may be obtained, either from the mother liquor of muriate of morphia by adding ammonia, or by digesting the insoluble part of opium in diluted acetic acid, and precipitating by ammonia. The impure narcotine is purified by solution in hot alcohol, with the aid of animal charcoal. On cooling, narcotine is deposited in crystals, which are insoluble in water and alkalies, soluble in alcohol, ether, and acids. Its salts are bitter, and crystallise with great difficulty.

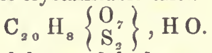
The very recent researches of Liebig, Wöhler, and Blyth, have made known a series of products of decomposition derived from narcotine, when acted on by peroxide of manganese and sulphuric acid, and also by bichloride of platinum. These our space will only permit us briefly to mention.

1. *Opianic acid.* $C_{20}H_9O_{10} = C_{20}H_8O_9, HO$. This acid crystallises in slender prisms, and forms soluble and crystallisable salts with baryta and the oxides of lead and silver, and with oxide of ethyle. When melted, opianic acid passes into an insoluble state, its composition remaining the same.

2. *Opiammon,* $C_{40}H_{17}NO_{16}$. This compound is derived from 2 eq. opianate of ammonia by the loss of 1 eq. ammonia and 4 eq. water. It is a pale yellow powder, which, by boiling with water, is converted into opianic acid and opianate of ammonia.

3. *Xanthopenic acid.* When opiammon is acted on by alkalies, it gives off ammonia and yields opianate and xanthopenate of potash. An acid separates the xanthopenic acid as a yellow flocculent precipitate. It forms salts of a fine yellow colour, but has not been fully examined. It contains nitrogen.

4. *Opiano-sulphurous acid,* $C_{20}H_8O_{11}S_2, HO$, is formed by the action of sulphurous acid on opianic acid, and is produced by the substitution of 2 eq. sulphurous acid for 2 eq. water. It has a bitter taste and forms crystallisable salts.

5. *Sulphopianic acid.*  $C_{20}H_8\left\{\begin{matrix}O_7\\S_2\end{matrix}\right\}, HO$. This acid is formed by the action of sulphuretted hydrogen on opianic acid, and is, in fact, opianic acid, in which 2 eq. of oxygen are replaced by 2 eq. sulphur. It is an amorphous yellow powder, which crystallises from alcohol. Its salts are soon decomposed, yielding sulphurets of the metals.

According to Wöhler, opianic acid is $(C_{20}H_6O_7, 2\,HO) + HO$; and in the two preceding acids the 2 eq. of water represented within the brackets are replaced by 2 eq. sulphurous acid and 2 eq. sulphuretted hydrogen. Opiammon, on this view, is $(C_{20}H_6O_7, 2\,HO) + (C_{20}H_6O_7, NH_3)$. He considers it probable that narcotine is a compound analogous to opiammon, and containing opianic acid.

6. *Hemipinic acid.* $C_{10}H_4O_5, HO$. This is a product of oxidation of opianic acid. 1 eq. anhydrous opianic acid, $C_{20}H_8O_9$, *plus* 1 eq. oxygen, is $C_{20}H_8O_{10} = 2(C_{10}H_4O_5)$. The hemipinic acid crystallises in regular four-sided prisms. It forms insoluble salts with the oxides of lead and silver.

7. *Cotarnine.* $C_{25}H_{13}NO_6$. This is a base formed along with opianic acid. 1 eq. narcotine, $C_{46}H_{25}NO_{14}$, and 7 eq. oxygen yield 1 eq. cotarnine, $C_{25}H_{13}NO_6 + 1$ eq. opianic acid $C_{20}H_9O_{10} + 1$ eq. carbonic acid $CO_2 + 3$ eq. water, $3HO$.

Cotarnine forms a deep yellow radiated mass, soluble in alcohol and in water. It is bitter and alkaline, and forms crystallisable double salts with the bichlorides of mercury and platinum.

8. *Humopinic acid* is a dark brown humus-like acid formed by the action of heat on narcotine. Its composition is not established with certainty, but resembles that of other similar bodies. It contains no nitrogen.

9. *Apophyllic acid.* This seems to be a product of decomposition of cotarnine. It forms crystals very like those of apophyllite and equally cleavable. When heated it yields an oily liquid, evidently quinoline. Its composition is not yet known, but it contains nitrogen.

10. *Narcogenine*, $C_{36}H_{19}NO_{10}$, is formed, along with opianic acid, when narcotine is not so far oxidised as to yield cotarnine. 2 eq. narcotine with 5 eq. oxygen yield 2 eq. narcogenine, 1 eq. opianic acid, and 3 eq. water. It forms a crystallisable double salt with bichloride of platinum, but when separated, it is resolved into narcotine and cotarnine. 2 eq. narcogenine, with 2 eq. oxygen, contain the elements of 1 eq. narcotine, 1 eq. cotarnine, and 1 eq. carbonic acid.

11. *Narcotinic acid.* When narcotine is heated with potash it forms a soluble compound which contains an acid, apparently isomeric with narcotine, or differing from it only by 1 or 2 eq. water. When this acid, which is called narcotinic acid, is separated from its salts, it rapidly passes into narcotine, so that it is unknown in a separate form. Its atomic weight seems to be half that of narcotine, so that 1 eq. narcotine probably forms 2 eq. of the acid.

Such is a very brief and imperfect account of the results of the recent researches of Wöhler and of Blyth on narcotine. They are of very great importance as indicating a method which may lead to the discovery of the true constitution of the alkaloids.

g. Chelidonine $C_{40}H_{20}N_3O_6$. This alkaliod occurs in *chelidonium majus*, along with *chelerythrine*. It is bitter, insoluble in water, and alkaline, forming crystallisable salts.

h. Chelerythrine found in the same plant, forms a grey powder which excites violent sneezing. With acids it forms red salts, which are narcotic and poisonous.

i. Glaucine. This alkaloid occurs in the leaves and stem of *Glaucium luteum.* It may be obtained in pearly scales; its taste is bitter and acrid, and it forms salts with acids. Its composition is not yet ascertained.

k. Glaucopicrine is found in the root of the same plant. It is bitter and forms salts of a bitter and nauseous taste. Its composition is unknown.

5. Alkaloids of the Solanaceæ, the Strychneæ, and other Vegetable Families.

a. Hyoscyamine. This base is found in *Hyoscyamus niger* and other species of hyoscyamus. Its composition is not yet known. It is extracted from the seeds by a difficult and tedious process, and may also be obtained, although with much loss, by distillation with potash, like conine. It is very prone to decomposition when in contact with mineral alkalies. It crystallises, when pure, in radiated groups of needles, but sometimes forms a viscid amorphous mass. When moist it has a stupefying smell like that of tobacco. It is very poisonous, causing, like conine, tetanic spasms. It dilates the pupil powerfully. It is fusible and volatile, but is partly decomposed when distilled. It dissolves in water, alcohol, and ether. It neutralises the acids, forming crystallisable salts which are very poisonous.

b. Daturine. This base is obtained from the seeds of *Datura stramonium.* It is, in preparation and properties, very analogous to hyoscyamine. It is, however, less soluble in water, and crystallises in fine brilliant prisms, from its alcoholic solution. It is fusible, volatile, and very poisonous, dilating the pupil. Its salts are crystallisable and very poisonous. Its precise composition is unknown.

c. Stramonine. This is another crystalline compound found in *stramonium.* It is crystallisable, volatile, soluble in alcohol and ether, insoluble in water. Its nature is uncertain and its composition unknown.

d. Atropine. $C_{34}H_{23}NO_6$? This alkaloid is the active principle of *Atropa belladonna.* It is obtained like daturine, and being equally prone to decomposition, much is always lost. It is sparingly soluble in water and ether, more soluble in alcohol. It crystallises in white silky prisms, and sometimes forms an amorphous mass like glass. It is very bitter, acrid, and poisonous, dilating the pupil like hyoscyamine and daturine. It is fusible and volatile, and neutralises acids, forming salts which are bitter, acrid, and poisonous, and which crystallise. These salts, from their very powerful action in permanently dilating the pupil, are very well adapted for medical use, being much more uniform than the extract.

e. Solanine. $C_{84}H_{78}NO_{28}$? This alkaloid occurs in many species of *Solanum*, as in *S. nigrum*, *S. dulcamara*, and in the potato, *S. tuberosum*. In the latter it is found especially in large quantity in the shoots, when the tubers have germinated in dark cellars. The shoots are extracted with dilute sulphuric acid, and the solution precipitated while hot by ammonia. The precipitate is purified by solution in alcohol. It forms a crystalline powder, very bitter and acrid, and highly poisonous, but not dilating the pupil. Its salts do not crystallise readily. There is some reason to suspect that the alkaloid of the shoots of potatoes may be distinct from that of the bittersweet, *Solanum dulcamara*.

f. Veratrine. $C_{34}H_{26}NO_{6}$? This alkaloid is found in *Veratrum sabadilla*, *V. album*, *&c.* It is extracted as atropine is, and is generally obtained as a crystalline powder, nearly white, very acrid and poisonous, exciting when introduced into the nostril violent and even dangerous sneezing. It is insoluble in water, but very soluble in alcohol, and may be obtained, by the spontaneous evaporation of its alcoholic solution, in prismatic crystals several lines in length. It is coloured red both by nitric and sulphuric acid.

Veratrine, in the form of tincture, and still more in that of ointment (1 drachm, or $\frac{1}{2}$ drachm to 1 oz. of lard), is now much used as an external application in neuralgia and obstinate rheumatic pains. Its effects in many cases are highly beneficial. In making the ointment the veratrine should first be rubbed with a few drops of alcohol to an impalpable powder, and the lard then added. If this be not done, the gritty particles of veratrine in the ointment cause so much irritation when rubbed into the skin as to prevent its use for any length of time. We are indebted chiefly to Dr. Turnbull for our knowledge of the valuable properties of this alkaloid.

g. Sabadilline. This name has been given by Conerbe to a second crystalline body found by him along with veratrine. It is alkaline, soluble in hot water, insoluble in ether, and forms crystallisable salts with acids. Conerbe states its formula to be $C_{20}H_{13}NO_{5}$; but, according to Simon, it is a compound of veratrine with resin, containing also resinate of soda.

h. Colchicine. This alkaloid is similar to veratrine, for which it was formerly taken. It is found in *Colchicum autumnale*. It is crystallisable, bitter, and very poisonous. Nitric acid colours it blue or violet. It is soluble in water, alcohol, and ether. Its salts are crystallisable, bitter, acrid, and poisonous. They might probably be used in medicine advantageously, instead of the very uncertain preparations of colchicum which are at present employed. In a very small dose, colchicine causes purging and vomiting. Its composition is unknown.

i. Aconitine. This alkaloid, the composition of which is unknown, is found in *Aconitum napellus*, and, probably, also in *A. ferox* and other species. It is obtained by the usual method, but, being very prone to suffer change, much is lost. It forms a crystalline powder, or occasionally a vitreous amorphous mass. It is in the highest degree bitter, acrid, and poisonous, and is said by Geiger to dilate the pupil. On the other hand, the plant contracts the pupil and causes numbness of the part to which it is applied, and Dr. Turnbull has obtained an aconitine possessing these properties in a very high degree. Either, therefore, there are two bases in the aconite, or, as is much more probable, the aconitine of Geiger having an action different from that of the plant, is a product of decomposition, while that of Turnbull is unchanged.

Turnbull's aconitine is an invaluable remedy in the same painful diseases in which veratrine is employed. It is unfortunately obtained in small proportion, and as yet is very expensive. A cheaper and more productive method of preparing it is a very great desideratum.

k. Delphine. $C_{27}H_{19}NO_2$? This alkaloid, analogous to veratrine, is found in *stavesacre, Delphinum staphysagria.* It has only been obtained hitherto as a yellowish white powder, not crystallised, very acrid, and poisonous. It forms neutral salts hitherto little examined. It may be used in the same affections and in the same manner as veratrine.

l. Staphisine. This is a substance found along with delphine, and said to be $C_{32}H_{23}NO_4$. It is acrid and poisonous, but is probably only a compound of delphine.

m. Emetine. $C_{37}H_{27}NO_{10}$? This is the active principle of ipecacuanha, the root of *Cephaelis ipecacuanha*. When pure, it is a white powder, alkaline, soluble in alcohol and in hot water, insoluble in ether. $\frac{1}{16}$ of a grain acts as an emetic. In a dose of from 2 to 4 grains it is poisonous. Its salts do not crystallise.

n. Chiococcine and *o. Violine* are two very similar alkaloids, found in *Chiococca ramosa* and *Viola odorata.* They are supposed by some to be emetine disguised by a little foreign matter.

p. Strychnine. $C_{44}H_{23}N_2O_8$, or $C_{44}H_{24}N_2O_8$. This alkaloid is found in nux vomica, the seeds of *Strychnos nux vomica*, in St. Ignatius's bean, the seed of *S. Ignatii*, in the wood of *S. colubrina*, and in the poison called *Upas tieuté*, derived from *S. tieuté*. It is extracted by decoction with dilute sulphuric acid, precipitating the decoction with milk of lime, and acting on the precipitate, after washing it with cold alcohol, by boiling alcohol, which on cooling deposits the strychnine in very regular transparent brilliant crystals. If brucine is present, it remains chiefly in the mother liquid, but the two bases may be separated by converting both into nitrates, and crystallising; the nitrate of strychnine crystallises readily, while the nitrate of brucine remains dissolved.

Strychnine is very insoluble, requiring 7000 parts of water. It is so bitter, that 1 part gives a very strong and persistent bitter taste to 40,000 parts of water. It dissolves in hot alcohol, although sparingly if the alcohol be pure, and is insoluble in ether. When pure, it is only coloured yellow by nitric acid; a trace of brucine causes it to be reddened by that acid. It forms crystallisable salts, which are intensely bitter. Their solutions are precipitated white by alkalies, by tincture of galls, and by iodide of potassium, in white crystals by sulphocyanide of potassium, and as yellow powders by solutions of gold and platinum.

Strychnine and its salts, especially the latter, from their solubility, are most energetic poisons. They produce spasmodic motions, and are used in very small doses as remedies in paralysis; they seem to have a specific action on the lower part of the spinal column. The average dose is $\frac{1}{12}$ of a grain. In the event of an overdose the best antidote is infusion of galls or strong tea, which also contains tannine.

q. Brucine. $C_{44} H_{25} N_2 O_7$. This alkaloid occurs along with strychnine in nux vomica, and also in the false angustura bark, the bark of *Brucia antidysenterica.* It is prepared as strychnine. Besides the methods above mentioned for separating the two bases, there is another, which is, to boil the mixture with water as long as it dissolves brucine, or till the strychnine is no longer reddened by nitric acid. Brucine forms large transparent crystals, which I have found to become opaque in closely stopped phials. It is very bitter and poisonous, but much less so than strychnine. It may be used for the same purposes in a rather larger dose. It is reddened strongly by nitric acid, and the red solution becomes violet on the addition of solution of tin. It is thus distinguished from strychnine and morphine. Its salts, for the most part, crystallise with facility.

r. Jervine. $C_{60} H_{45} N_2 O_3$. This alkaloid is found in white hellebore, *Veratrum album,* along with veratrine, from which it is separated easily, as it crystallises first from the alcoholic solution; and its sulphate is also far less soluble than that of veratrine. It forms a crystalline powder, fusible, insoluble in water, soluble in alcohol, and forming with sulphuric, nitric, and hydrochloric acids, very sparingly soluble salts, so that the solution of the acetate is precipitated by these three acids.

s. Curarine. This alkaloid is obtained from the South American poison called *curari*, which is derived from some plant of the family Strychnea. It is a deadly poison when introduced into a wound, but may be swallowed with impunity. The curarine forms a yellowish amorphous bitter mass, which is more poisonous than the curari which yields it. Its salts are bitter, but do not crystallise.

t. Corydaline. $C_{34}H_{22}NO_{10}$? Found in the root of *Corydalis bulbosa* and *C. fabacea.* It forms a light grey powder, very soluble in alcohol, which deposits it in crystals. It is reddened by nitric acid, and forms crystallisable salts with acetic and sulphuric acids.

u. Carapine. Found in *Carapus guianensis.* It is a white pearly fusible powder, very bitter, soluble in water and alcohol, insoluble in ether, forming crystallisable salts with hydrochloric and acetic acids.

v. Cusparine. Found in the true angustura bark, that of *Bonplandia trifoliata* or *Cusparia febrifuga.* It forms fusible octahedral crystals, sparingly soluble in water, very soluble in alcohol.

w. Daphnine. Occurs in the bark of *Daphne gnidium* and *D. mezereon.* It is obtained by distilling the infusion with magnesia. It is alkaline and acrid, and forms crystallisable salts with nitric and sulphuric acids, according to Vauquelin. Baer and Gmelin could not obtain it.

x. Bebeerine is the active principle of the bark of the *bebeeru* tree of Guiana, which seems to be analogous to quinine. It has not been obtained crystallised or colourless, but as a brown mass, the composition of which is not yet ascertained. Bebeerine and its salts are bitter and highly febrifuge. Dr. Douglas Maclagan and Mr. Tilley have found its composition to be the same as that of morphine, namely $C_{35}H_{20}NO_6$.

y. Sanguinarine is found in *Sanguinaria canadensis.* It forms a grey powder, which is alkaline and yields red salts. It excites sneezing, and is possibly identical with chelerythrine.

z. Azadirine, found in *Melea azadirachta* is alkaline, forms a crystallisable salt with sulphuric acid, and is powerfully febrifuge.

aa. Capsicine is the active principle of the capsules of *Capsicum annuum* or cayenne pepper. It has a resinous aspect and a burning taste, but when quite pure may be crystallised. It forms crystallisable salts with acetic, nitric, and sulphuric acids. It is soluble in alcohol, insoluble (when pure) in ether and in water.

bb. Crotonine occurs in the seeds of *Croton tiglium*, and may be obtained from croton oil by boiling it with water and magnesia. It forms crystals, which are fusible, soluble in alcohol, insoluble in water. It forms crystallisable salts with sulphuric and phosphoric acids.

cc. Buxine. Occurs in Boxwood bark. It forms a bitter, brown, amorphous mass, soluble in alcohol, alkaline, and forming a crystalline sulphate. It excites sneezing.

dd. Apyrine. Found in *Cocos lapidea.* It is a white alkaline powder, forming crystalline salts with acids.

ee. Cynapine. From *Æthusa cynapium.* It is crystallisable, soluble in water and alcohol, and forms a crystalline sulphate

ff. Cissampeline, or *Pelosine*, from Cissampelos Pareira, is a white powder, soluble in alcohol and ether; alkaline, forming soluble salts, of which the hydrochlorate crystallises.

gg. Oxyacanthine and *Berberine* are two bitter substances found in the barberry, *Berberis vulgaris.* The former is decidedly alkaline, and forms crystallisable salts. The latter is bitter, yellow, and feebly, if at all, alkaline. It crystallises, and is used in dyeing. Its formula is $C_{33}\ H_{18}\ N\,O_{12}$.

hh. Surinamine and *Jamaicine* are two alkaloids, found in *Geoffrœa Surinamensis* and *G. inermis.* Both are crystallisable, and form crystallisable salts; those of the latter are precipitated by tannine and corrosive sublimate.

ii. Piperine, $C_{34}\ H_{19}\ N\,O_{6}$. This compound is found in pepper, *Piper nigrum*, and *P. longum.* It is crystallisable, soluble in alcohol, very pungent. It is a feeble base, but does form salts, especially double chlorides, containing hydrochlorate of piperine.

kk. Menispermine and *Paramenispermine* are found in *cocculus indicus*, the seed of *Menispermum cocculus.* Menispermine is white, fusible, crystallisable, and forms salts, of which the sulphate crystallises. Its formula is $C_{18}\ H_{12}\ N\,O_{2}$.

Paramenispermine has the same composition. It is less fusible, but sublimes at a high temperature. It does not appear to form definite salts. Both are insoluble in water, and soluble in alcohol; and paramenispermine is insoluble in ether.

ll. Harmaline, $C_{24}\ H_{13}\ N\,O$. This alkaloid occurs united with phosphoric acid in the seeds of *Peganum Harmala.* It forms brownish-yellow prisms, bitter, astringent, and acrid, very soluble in alcohol, little soluble in water or ether. It is fusible, and partly volatile. It forms, with acids, yellow crystallisable salts. By oxidising agents, harmaline is transformed into a red matter, which forms red salts with acids. The harmala red of commerce is the powder of the seeds already transformed into the phosphate of the red harmaline. It is used in dyeing, especially in giving to silk every shade of red, rose-colour, and pink. It is produced abundantly in the steppes of southern Russia, and is little known out of that country.

mm. Theobromine, $C_9 H_5 N_3 O_2$. This is a crystalline compound, found in cacao, the seed of *Theobroma cacao.* It can hardly be called an alkaloid. It is very analogous to the next substance, caffeine.

nn. Caffeine, $C_8 H_5 N_2 O_2$. SYN. *Théine. Guaranine.* This remarkable compound is found in *coffee*, in *tea*, in *guarana officinalis*, or *paullinia sorbilis*, and in *ilex paraguayensis.* It is best obtained by adding to a decoction of tea a slight excess of acetate of lead, and evaporating to dryness the filtered liquid. The dry mass mixed with sand, is heated in the apparatus described for benzoic acid, when caffeine is obtained in crystals. Tea yields more than 1 per cent.

Caffeine forms fine white prisms, of a silky lustre, which are soluble in water, alcohol, and ether, bitter, fusible and volatile. It is a feeble base, but forms with hydrochloric acid and sulphuric acid, salts which yield very large crystals.

It is very remarkable, that caffeine should approach so nearly in composition to alloxan and alloxantine. Anhydrous alloxan, plus 1 eq. water, is $C_8 N_2 H_5 O_{11}$, and alloxantine is $C_8 N_2 H_5 O_{10}$, while caffeine is $C_8 N_2 H_5 O_2$, differing from the one by 9, from the other by 8 eq. oxygen.

Further, caffeine, $C_8 N_2 H_5 O_2$, added to 9 eq. water and 9 eq. oxygen (that is, to $H_9 O_{18}$), is $C_8 N_2 H_{14} O_{20}$, which is equal to 2 eq. taurine, a nitrogenised principle derived from the bile. We shall hereafter see how close a connection can be traced between the bile and the urine; but in the meantime it is a most striking fact, that tea, coffee, Paraguay tea, and guarana, are all used by different and distant nations for the same purpose, namely, as a refreshing and gently stimulating drink, which notoriously promotes the vital functions, while all these plants contain the very same compound, and that one allied to the bile and the urine, the chief products of the vital metamorphosis. The quantity of caffeine in tea is indeed small, but not too small to have a perceptible influence on the system. Peligot has shown that gunpowder-tea contains 6 per cent. of théine (caffeine).

By the action of nitric acid, caffeine yields a crystalline nitrogenised compound, *nitrothéine.*

Besides caffeine, or théine, tea contains 14 or 15 per cent. of caseine, and the leaves are therefore nutritious, when eaten, as they are, by some oriental nations.

The following substances have been noticed as alkaloids, but are very little known: *Castine* in *Vitex agnus castus; Cicutine* in *Cicuta virosa; Chœrophylline* in *Chœrophyllum bulbosum; Esenbeckine* in *Esenbeckia febrifuga; Digitaline* in *Digitalis purpurea; Eupatorine* in *Eupatorium cannabinum; Euphorbine* in *Euphorbium; Convolvuline* in *Convolvolus scammonium;* and *Pereirine* in *Pereyra bark.*

We now come to a class of compounds, very widely distributed in the vegetable kingdom, but not exhibiting the same varieties as the classes hitherto described, and not characterised by the same marked properties. This is the class of neutral or indifferent non-azotised bodies, which are never poisonous, hardly even possessed of medicinal properties, and exhibit no striking chemical characters. It includes starch, gum, or mucilage, pectine or vegetable jelly, and woody fibre or lignine, with their derivatives. We can only describe them briefly.

INDIFFERENT NON-AZOTISED COMPOUNDS.

1. Starch. $C_{12} H_{10} O_{10}$.

This very important compound is universally diffused in the vegetable kingdom. It occurs in seeds, as in those of wheat and other cerealia, and also in the leguminosæ; in roots, as in the tubers of the potato; in the stem or pith of many plants, as in Sagus Rumphii; in some barks, as that of cinnamon; and in pulpy fruits, such as the apple. Finally, it is contained in the expressed juice of most vegetables, such as the carrot, in a state of suspension, being deposited on standing.

It is chiefly extracted from wheat-flour (*common starch*); from potatoes (*potato starch*); from the root of *Jatropha manihot,* (*tapioca*); from that of *Maranta arundinacea* (*arrow root*); from the stem and pith of *Sagus farinifera Rumphii* (*sago*); the substances known by these different names being all essentially the same.

When flour is kneaded with water in a cloth, the water carries off the starch in suspension, and deposits it on standing, leaving behind the gluten. By a similar process starch is purified from the cellular substance and other matters mixed with it in potatoes, which are rasped, and then treated with water as above. Sago, being finally dried at a somewhat high temperature, acquires a horny and translucent appearance.

Pure starch is a snow-white powder, of a glistening aspect, which makes a crackling noise when pressed with the finger. It is composed of transparent rounded grains, the size of which varies in different plants. Those of the potato are the largest, those of the leguminosæ, as peas, are very small, and those of wheat and rice are the smallest. Starch is insoluble in cold water, alcohol, and ether; but when heated with water it first becomes viscid, and is then converted into a kind of solution, which, however, is not complete, but is rather formed by the swelling of the grains of starch into a mucilaginous mass. On cooling, the whole forms a stiff, semi-opaque jelly. If dried up, this yields a translucent mass, which softens and swells into a jelly with water, like tragacanth. The solution, or mixture of starch and water, has the remarkable property of striking a deep blue colour with free iodine. This appears to be owing not so much to a chemical or definite combination, as to the mechanical division of the iodine; there is even reason to think that the blue colour is that of iodine finely divided, adhering to the starch as a dye does to the fibres of cloth.

When starch is warmed with water, to which has been added either some infusion of malt or some diluted acid, the viscidity of the mixture disappears, and the fluid solution is no longer coloured blue by iodine. As soon as this is the case, the whole of the starch has disappeared, and has been converted into a soluble gum called *dextrine*, from its power of causing the plane of polarisation to deviate to the right. According to the proportion of malt or of acid, and the temperature employed, the change is more or less rapid; and when the action is continued the dextrine is in its turn converted into *glucose*, or grape-sugar, which from this circumstance is also called starch-sugar.

In contact with oil of vitriol, starch appears to form a compound or coupled acid, *sulphoamidic acid*. Strong nitric acid, rubbed up with potato starch, dissolves it, forming a viscid liquid, from which water precipitates a white compound, called *xyloidine*. This compound has some of the properties of gum-tragacanth, but it contains the elements of nitric acid, and has not yet been fully investigated. According to Pelouze, its formula is $C_6 H_4 O_4 + N O_5$; according to Ballot, it is $C_{15} H_{12} N O_{16}$. When starch is distilled with moderately-strong sulphuric acid, it yields carbonic acid, formic acid, and a pungent volatile oil, hitherto very little examined.

The blue compound of iodine and starch is best prepared by adding to the liquid filtered from the viscid paste obtained by boiling starch with water, first iodide of potassium, and then solution of chlorine, as long as it causes a blue precipitate, which is to be washed till the water passes deep blue, and dried in vacuo.

Its colour is so intense as to be nearly black. It does not appear to be a compound in definite proportions. The best method of using starch as a test for iodine in mineral waters, &c., is to add to the water some starch paste, and then a little nitric acid or chlorine. The latter is best added in the form of gas, its weight allowing it to be poured like water; while in this way we are less likely to add an excess which would destroy the blue colour. Or we may place in the bottom of a phial the liquid to be tested, adding a little oil of vitriol, and suspending from the stopper a slip of paper moistened with starch paste. After a time, if iodine be present the paper will exhibit a tinge of blue. By these tests $\frac{1}{40000}$th part of iodine in a liquid may be detected.

With bromine, starch forms an orange yellow precipitate, which cannot be dried without decomposition.

Dextrine is best obtained by heating to about 120° a mixture of 20 parts of starch paste and 1 part of strong infusion of malt, until iodine no longer colours the mixture blue. The addition of strong alcohol now precipitates the dextrine as a thick syrup, while any sugar remains dissolved. When dried, dextrine much resembles gum, from which, however, it differs in the extreme facility with which it is converted into sugar when warmed with dilute sulphuric acid or infusion of malt, and by not yielding mucic acid when acted on by nitric acid. The composition of dextrine is the same as that of starch. In fact, dextrine is supposed by some to be the substance which is contained in the grains of starch, inclosed in an insoluble membrane, which is burst in the process of conversion of starch into dextrine, or solution of starch, by means of acids and infusion of malt. The substance present in the malt which has the property of effecting this change, is called *diastase*. It contains nitrogen.

According to other observers, the grains of starch are composed of concentric layers of one and the same substance (dextrine ?), the outer layer being insoluble in water. As starch is found to contain a small proportion of a matter analogous to wax or to caoutchouc, we may suppose that the presence of this matter in the outer layer is the cause of its insolubility, or that the whole mass of the grains is, by its means, rendered insoluble, and endowed with the property of swelling up with water to a paste or jelly. Dextrine will then be the purified, and consequently soluble, matter of starch. If the outer coat be different from the contents of the grains, it has still the same composition; for analysis shows no difference between starch, dextrine, and the insoluble matter left on the filter when starch is boiled with diluted acids.

Leiocome. This name is given to a substance having the properties of gum, which is prepared by simply roasting or torrefying starch at about 300°. It is, in fact, capable of being used instead of gum in calico-printing, and is made on the large scale. It has a yellowish-brown colour. It is probably dextrine, more or less pure, generally containing some undecomposed starch. When well made it dissolves in cold water like gum.

Inuline. $C_{24}H_{18}O_{18}$? $C_{32}H_{24}O_{24}$? $C_{24}H_{21}O_{21}$? This is a substance analogous to starch in the roots and tubes of *inula helenium*, *dahlia variabilis*, *helianthus tuberosus*, and many other synantherous plants, which do not yield ordinary starch.

It is extracted from the roots by boiling water, and is deposited by the concentrated decoction as a brittle white mass, formed of crystalline grains, or as a fine powder. It is tasteless, insoluble in cold, very soluble in hot water. Diluted sulphuric acid, with the aid of heat, rapidly converts it into grape-sugar, from which, like starch, it differs only by a certain amount of the elements of water. This may be seen by the above formulæ, which represent inuline from different plants, as it exists in its compounds with oxide of lead. It would appear to differ in different vegetables, but always retaining the character of this class of bodies, namely, the presence of hydrogen and oxygen in the proportions to form water. Iodine colours it slightly brown.

Lichenine, $C_{12}H_{10}O_{10}$. This is a variety of starch found in *lichen islandicus*, or iceland moss. It forms, when pure, a nearly colourless, tasteless mass, which swells up into a transparent jelly with cold water, and dissolves entirely in hot water. When its solution is boiled, it forms pellicles, like milk, which adhere to the vessel. Its solution is not coloured by iodine, but the jelly is rendered blue by that test. By diluted and boiling sulphuric acid it is converted into sugar ; by nitric acid into oxalic and saccharic acids. It has the composition of starch.

Saponine is the name given to a variety of starch obtained from the root of *saponaria officinalis*. Its properties are little known.

2. Gum.

This name was formerly given to almost all exudations from plants. It is now limited to certain rather abundant substances, which are solid, uncrystallisable, transparent, or translucent, colourless, or nearly so, tasteless, inodorous, soluble in water, or at least softening in it, and insoluble in alcohol, ether, fat and volatile oils. They yield mucic acid when acted on by nitric acid. They may be divided into gums, which dissolve in cold water (arabine, mucilage), and gums which only swell up to a jelly (tragacanth or bassorine, cerasine, pectine). Arabine and cerasine contain oxygen and hydrogen in the proportion to form water: the other gums are nearly analogous in composition.

Arabine, or gum arabic, is found as an exudation from several species of acacia. What is called gum senegal is essentially the same. It is nearly colourless, transparent, hard, and brittle, and has a mild taste. It is very soluble in cold water, and forms a viscid mucilage, from which alcohol precipitates the gum. The diluted solution is precipitated by silicate of potash, subacetate of lead and protonitrate of mercury. When a mixture of gum, water, and sulphuric acid is kept for some time at a temperature near boiling, it is converted into grape sugar. The composition of gum is $C_{12} H_{11} O_{11}$, that is, the same as that of cane sugar, which accounts for the transformation. Arabine yields 2 or 3 per cent. of ashes, containing a good deal of lime.

Mucilage is the name given to a substance resembling gum, found in many vegetables, such as *linseed, althœa,* and others. It differs from arabine in being less hard when dry, and less transparent. It would appear, however, that the mucilage of althæa-root is essentially starch enclosed in cells formed of woody fibre or cellulose. The different mucilages are resolved into grape sugar by being heated with dilute sulphuric acid, and therefore may be considered as containing, like starch and arabine, water plus carbon. Since all these mucilages contain much mineral matter, the mucilage of linseed, for example, leaving 11 per cent. of ashes rich in lime, it is probable that their peculiar qualities depend on the presence of phosphate of lime or other salts of lime, disguising either starch or arabine.

Bassorine is the name given to a substance which forms the chief part of *gum tragacanth* and of *gum bassora*, and also, according to some, of *salep,* a mucilaginous substance, obtained from the bulbs of *orchis mascula.* According to Schmidt, however, salep is really formed of swelled up grains of starch.

Pure bassorine resembles arabine in appearance, but is less transparent, and instead of dissolving in cold water, only swells up to a very great extent, forming a viscid mass. Its composition is analogous to that of arabine, and by digestion with diluted sulphuric acid, it is transformed, like salep, into grape sugar and cellulose. *Cerasine* is the name given to that part of the gum of the cherry, plum or almond trees, which is insoluble in cold water. It is probably identical with bassorine, or with salep.

During what is called the viscous fermentation, which takes place in certain sweet vegetable juices, as that of beet-root, there is formed, along with lactic acid and mannite, a mucilaginous compound, which causes the vicidity. When dried, it has nearly the characters and composition of arabine.

Pectine is the substance which causes the juice of some pulpy fruits, as apples and pears, to coagulate or gelatinise when mixed with alcohol, by which the pectine is precipitated. When dried, it resembles gum or isinglass, and forms a jelly with water. By the action of nitric acid it yields oxalic and mucic acids. It generally yields about 8 per cent. of ashes, containing much phosphate of lime. In contact with alkalies, it is transformed into pectic acid. *Pectic acid* is easily obtained from many vegetables, as, for example, rasped carrots, by washing them well with distilled water, and then boiling 50 parts of the squeezed residue with 300 of water and 1 of potash. The pectate of potash is deposited as a jelly in the filtered liquid on cooling. Either this salt or the pectate of lime may be decomposed by diluted hydrochloric acid, which leaves the pectic acid as a jelly, which dries up into transparent laminæ, insoluble in water but very soluble in alkalies. From these solutions acids precipitate it as a jelly. In this form it is slightly soluble in boiling water, but the solution gelatinises on the addition of acids, salts, alcohol or sugar. It is supposed not to exist ready formed in the plants, but to be produced by the action of alkalies on pectine.

The alkaline pectates, when dry, form gummy solids, soluble in water. Alcohol causes the solution to gelatinise, and even an excess of potash or soda has the same effect. The earthy and metallic pectates are gelatinous and insoluble. When dried, pectine, pectic acid, and all the pectates, assume a cellular structure, so to speak.

The jelly formed in currant juice as well as other juices by the addition of sugar is pectine or pectic acid. The boiling of such juices probably promotes the formation of jelly; for it has been shown that when the insoluble part of unripe currants, after being washed, is boiled with water acidulated with a vegetable acid, a considerable quantity of pectine is formed, probably by a transformation of the cellular tissue.

The composition of pectic acid is not fully ascertained. According to Regnault it is $C_{12}\,H_8\,O_{11}$, or $C_{12}\,H_7\,O_{10}$, HO. According to Mulder, it is $C_{12}\,H_8\,O_{10}$. But the researches of Chodnew have led him to adopt the formula $C_{28}\,H_{18}\,O_{24}$, $2\,HO = C_{28}\,H_{20}\,O_{26}$. In all the formulæ there is an excess of oxygen over hydrogen.

The whole subject of the mucilaginous compounds, including pectine and pectic acid, is still very obscure and requires renewed investigations.

Apiine is a substance analogous to pectine, found in parsley, *apium graveolens. Glycyrrhizine* is the name given to a substance resembling both sugar and gum, which is the chief ingredient in liquorice, the juice of the root of *glycyrrhiza glabra.* It is soluble in hot water, and gelatinises on cooling. Its taste is sweet and also acrid, but it does not, like sugar, undergo the vinous fermentation. Its formula is said to be $C_{16} H_{12} O_6$.

Sarcocolline is a gummy matter found in the sarcocolla of commerce, which is the dried juice of *penœa mucronata.* It is soluble in alcohol and water, and has a taste both sweet and bitter. Formula $C_{22} H_{19} O_{10}$? or $C_{40} H_{32} O_{14}$?

3. Woody Fibre.

The skeleton of plants, after everything soluble in water, alcohol, ether, diluted acids, and diluted alkalies has been removed, is called woody fibre. It varies in aspect and in composition as obtained from different plants. That of box or willow, when dried, is $C_{12} H_9 O_9$; that of oak is $C_{36} H_{22} O_{22}$; and that of beech is intermediate between these two. All varieties, however, may be represented as composed of carbon plus water.

Recent researches have shown that wood is composed of two parts: 1. *cellulose*, which forms the parietes of the vegetable cells; and 2. *lignine*, which fills those cells, or forms an incrustation on their walls. The latter dissolves in strong nitric acid, the former is left undissolved. Again, oil of vitrol dissolves cellulose without blackening, and appears to convert it into dextrine, with which it agrees in composition; while lignine separated from cellulose is said to contain $C_{35} H_{24} O_{20}$.

By the continued action of acids or of hot alkalies, woody fibre yields a substance which is coloured blue by iodine. Linen, cotton, or paper, all of them different forms of woody fibre, when moistened with pretty strong sulphuric acid, are converted apparently first into dextrine, and afterwards into grape sugar. When heated with a more diluted acid, linen yields an amylaceous pulp hardly soluble in water, the composition of which is $C_{12} H_{10} O_{10}$.

When exposed to air and moisture, wood undergoes eremacausis, being slowly converted into a friable mass, which contains a larger proportion of carbon than the original wood. It would appear that the oxygen of the atmosphere combines with the hydrogen, and that carbon and oxygen are given off from the residue as carbonic acid, CO_2. As the residue is found still to consist of carbon and water, it is evident that for every equivalent of carbon removed, there are separated 2 eq. of oxygen and hydrogen, so that the proportion of carbon to water in the residue is constantly increasing. Woody fibre $C_{36} H_{22} O_{22}$ will thus yield first a residue of $C_{35} H_{20} O_{20}$; then $C_{34} H_{18} O_{18}$, $C_{33} H_{16} O_{16}$, and so on. When air is left in contact with moist wood, its oxygen is removed and replaced by an equal volume of carbonic acid. This is one chief source of the insalubrity of marshy districts; and the effect is seen still more strikingly in the case of houses which have been submerged in an inundation, which are very unwholesome as long as the wood is moist.

The tendency of wood to decay is checked or destroyed by acids and many salts, especially corrosive sublimate. Out of contact of air, moist wood putrefies, yielding a white friable residue, containing less carbon than the wood. One specimen yielded $C_{33} H_{17} O_{20}$, while the corresponding product of eremacausis above mentioned is $C_{35} H_{20} O_{20}$, and the wood $C_{36} H_{22} O_{22}$.

The composition of brown coal is analogous to that of wood partially decayed, but subjected to changes of the nature of putrefaction, as well as to eremacausis. Two specimens of brown coal yielded $C_{33} H_{21} O_{16}$ and $C_{32} H_{15} O_{9}$.

All the above products of decomposition of wood may be derived from oak wood, $C_{36} H_{22} O_{22}$, by the fixation of oxygen, and the separation of water and carbonic acid.

When the substance called mould, which contains the debris of decayed vegetable matter, is boiled with alkalies, the filtered solution deposits, on the addition of acids, a brown precipitate, which has been called ulmine, humus, humine, geine, ulmic acid, humic acid, and geic acid. It is generally admitted that this precipitate is a product of the action of the alkali on the decayed vegetable matter, and the name of humus, humine, or geine is given to the substance which is believed to yield the humic acid. But this humus has not been isolated, and is not known.

Mulder examined the precipitates obtained from a variety of different sources, decayed wood, turf, peat, mould, &c. With one exception, he found all to contain introgen, varying from 2.5 to 7 per cent. It is evident that these substances are vegetable matter in different stages of decay. Mulder considers these precipitates as compounds of water, or water and ammonia, with three different acids: 1. acid of mould $C_{40} H_{12} O_{14}$: 2. humic acid, $C_{40} H_{12} O_{12}$: 3. ulmic acid, $C_{40} H_{14} O_{12}$.

When sugar is boiled with diluted acids, it yields brown substances analogous to, if not identical with, these acids of Mulder.

It is important to observe the general presence of ammonia in mould, &c. This ammonia has no doubt been absorbed from the air in great part; and this will explain the favourable influence which these substances exert on vegetation. They act also in furnishing, by their slow decay, a continual supply of carbonic acid.

Crenic acid and *Apocrenic acid* are two brown extractive matters, analogous to the preceding, and derived from decaying vegetable matter, which are found in certain mineral waters. They both appear to contain nitrogen.

PRODUCTS OF THE DISTILLATION OF WOOD.

When wood is heated in close vessels, it gives rise to an immense variety of products, according to the kind of wood and to the presence or absence of resinous or oily matters. In all cases these are formed gaseous, liquid, and solid products, with a residue of charcoal.

The gases are carbonic acid, carbonic oxide, olefiant gas and marsh gas. The liquids are partly soluble in water, partly insoluble. The latter constitute the tar, and are of a semifluid consistence.

The substances soluble in water are, besides water itself, acetic acid, acetone, pyroxylic spirit (hydrate of oxide of methyle), acetate of oxide of methyle, lignone, xylite and mesite.

The oily substances, insoluble in water, are very numerous, including creosote, picamar, eupion, capnomor, &c. Along with these are the compounds which at the ordinary temperature are solid, such as paraffine, naphthaline, cedriret, pittacall, pyréne, chryséne, and pyroxanthine. The last mentioned, being very volatile, chiefly accompanies the acetic or pyroligneous acid.

1. Volatile Products, soluble in water.

Acetic Acid. This is one of the chief products of the distillation of woods. Its mode of purification and its properties have been already described. As prepared from this source, it is often called pyroligneous acid. The crude or impure acid is highly antiseptic ; not only because vinegar, like most acids, is so, but also because it contains much creosote dissolved. Hence it not only preserves meat, but gives to it a powerful and agreeable smoked flavour.

Pyroxylic Spirit. This name is given to the spirituous liquid, distilled from the crude pyroligneous acid before the latter is purified. It is a mixed fluid, the chief component being hydrated oxide of methyle, which is accompanied by acetate of oxide of methyle, unless it has been rectified with quicklime, which decomposes the latter. *Lignone* is the name given to a volatile liquid, somewhat resembling alcohol, observed in pyroxylic spirit by Gmelin and Liebig. Its formula is not ascertained, since it does not, as far as we know, form definite compounds, from which its equivalent might be deduced. *Xylite* is another similar volatile liquid, which, according to Schweitzer, is $C_{12} H_{12} O_5 = 2 (C_2 H_3 O) + (C_8 H_6, O_3) = 2 \, Mt O + Ac_2 O_3$; that is a compound of 2 eq. oxide of methyle and 1 eq. of a sesquiacetylic acid. When acted on by potash, it yields a crystalline salt $C_{18} H_{15} O_7, KO$, while hydrated oxide of methyle separates. An excess of potash causes the formation of three products: *xylitic naphtha*, $C_{12} H_{12} O_3$; *xylitic oil*, $C_{12} H_9 O$; and *xylitic resin*, $C_8 H_6 O$. When distilled with sulphuric acid, xylite, if moist, yields a new compound, *mesiténe*, a volatile liquid, $C_6 H_6 O_3$. If anhydrous, it yields, besides, another compound, *methol*, a less volatile liquid, which appears to be a carbo-hydrogen, $C_4 H_3$; isomeric with acetyle, if it be not that radical. *Mesite* is another volatile ethereal liquid found in pyroxylic spirit, which, according to Schweitzer, is $C_6 H_6 O_2$; isomeric with acetone. He considers it as composed of oxide of methyle and oxide of acetyle, $C_2 H_3 O + C_4 H_3 O = Mt O + Ac O$. The liquid called mesite by Reichenbach would appear to be acetate of oxide of methyle, $Mt O + Ac O_3$, mixed with a more highly carbonised body, apparently composed of $C_{26} H_{25} O_{15}$. This latter is resolved by the action of lime into 3 eq. acetic acid ($C_{12} H_9 O_9$), and a volatile liquid, $C_{14} H_{16} O_6$. Along with the above, another liquid appears to occur in the mesite of Reichenbach, the composition of which is $C_{21} H_{23} O_{10}$. In addition to all the liquids above mentioned, as occurring in pyroxylic spirit, acetone is frequently found.

The very great similarity in properties of so many substances, namely, hydrated oxide of methyle, acetate of oxide of methyle, lignone, xylite, mesite, and acetone, is worthy of notice. Most of these liquids have nearly the same density and boiling point; they are all inflammable, and their solubility in water is nearly equal. Hence they all occur mixed, and are with great difficulty separated, so as to obtain each in a state of purity; indeed in most of them we cannot be sure that this has yet been accomplished. It is highly probable, that, like the two first, all the rest will be found to be compounds of methyle. Our knowledge on the subject is still very limited.

The purified pyroxylic spirit, or hydrated oxide of methyle, has been already fully described, along with its chief derivatives.

2. Volatile Oily Products, insoluble or sparingly soluble in Water.

a. Creosote (from κρεας, flesh, and σωζω, I preserve). This is one of the most important products of the distillation of wood.

It is found, partly dissolved, in the pyroligneous acid, partly along with other oils, in the tar. When the crude pyroligneous acid is saturated at 167° with dry sulphate of soda, an oil separates, which contains much creosote. In like manner, by the rectification of tar, an oil of tar is obtained, the heavier portions of which contain a good deal of creosote. These oils are neutralised with carbonate of potash, and the fluid thus deprived of acid is distilled with water. The distilled oil is acted on by dilute phosphoric acid to remove ammonia and, probably, traces of oily bases, again distilled, and dissolved in aqua potassæ, Sp. G. 1·12, which dissolves the creosote, along with portions of other oils, but separates a good deal of eupion, &c. The alkaline solution is now supersaturated with dilute sulphuric acid, (after having been boiled in the air till it has become dark brown,) when the impure creosote separates. It is again rectified, and the treatment with potash, boiling, addition of sulphuric acid, and rectification repeated till the rectified oil dissolves entirely in weak potash, and this alkaline solution on being boiled acquires only a slight tinge of colour. It is then finally rectified, and is pure when it continues colourless on being kept. The tar of peat appears to be very rich in creosote, and it also occurs in coal tar. Good tar, from beech wood, is said to contain from 20 to 25 per cent.

Pure creosote is a colourless transparent liquid, of a high refractive and dispersive power, of a tolerably fluid but oily consistence. Its Sp. G. is 1·037, according to Reichenbach, its discoverer, and other chemists; but there is some discrepancy on this point, Dr. Christison having always found it as high as 1·060 and upwards. Its boiling point is 397°. It gradually becomes coloured brown when kept, unless absolutely pure. Creosote has a very strong, peculiar, persistent smell of smoke, analogous also to that of castoreum, not fetid, but unpleasant when concentrated. Its taste is burning, with a sweetish aftertaste. It disorganises the skin, causing a white spot, where the cuticle soon peels off, without inflammation. When applied to the interior of the mouth and to the tongue it smarts strongly, whitening and disorganising the cuticle.

Internally it is a powerful poison, but in a small dose may be employed advantageously in some cases of vomiting and disease of the mucuous membrane. It is given much diluted with water. Externally, it may be employed, either in the form of aqueous solution, of ointment, or pure, as a styptic, and is a valuable application to indolent ulcers, and to many chronic cutaneous affections. Pure creosote, applied to the hollow of a decayed tooth, so as to touch the exposed nerve, instantly relieves, in many cases, the most violent toothache. It acts apparently by coagulating the secretions, and thus forming a covering for the nerve.

Creosote dissolves in about 80 or 100 parts of water, and is exceedingly soluble in alcohol and in acetic acid. These solutions have the smell, taste, and antiseptic power of the creosote.

Creosote possesses a singular antiseptic power. Flesh of all kinds, if steeped for a few hours in a weak solution of creosote, becomes unsusceptible of putrefaction; and the same effect is produced when the flesh is exposed to the vapour of creosote. This is the reason why the smoke of wood possesses antiseptic properties: smoked meat or fish is merely meat or fish which has absorbed the vapour of creosote from the smoke in which it has been suspended. The creosote appears to act on flesh, &c. in virtue of its remarkable power of coagulating albumen, which also accounts for its styptic action. Tongues and hams may be smoked and effectually cured by immersing them for 24 hours in a mixture of 1 part of pure creosote and 100 of water or brine; and when thus prepared, they have the delicate smoked flavour observed in reindeer tongues, as usually cured by smoking.

Owing to the difficulty of obtaining creosote quite pure, its composition is hardly ascertained with certainty. According to Deville, whose researches are the most recent, it may be regarded as the alcohol, so to speak, of the series of benzoyle. His analyses lead to the formula $C_{14} H_8 O_3$ or $C_{14} H_7 O_2, HO$; but I cannot ascertain whether this is the formula he adopts.

It is particularly to be noticed, that there is a very great resemblance between creosote and carbolic acid (or hydrate of phenyle, $C_{12} H_5 O, HO$), a substance obtained from coal tar, and which will soon be described. So great is this resemblance, that I am almost inclined to consider creosote as a somewhat impure carbolic acid. The taste, smell, density, (according to some), boiling point, solubility in water, &c., poisonous and antiseptic action, of these two bodies, are the same. Both combine with alkalies, forming crystallisable compounds, and, what is more important, their composition in 100 parts is almost identical. The chief differences seem to be, that carbolic acid may be obtained in crystals, which, however, on contact with the air instantly liquefy and retain the liquid form, without any appreciable change of composition, apparently from the effect of a trace of moisture. Also, the salts of carbolic acid with bases are more easily formed and more permanent than those of creosote. A splinter or shaving of fir wood, dipped into carbolic acid and then into nitric or muriatic acid, becomes first blue and then brown ; which does not appear to be the case with creosote. But Laurent has recently shown, that creosote, when acted on by a mixture of hydrochloric acid and chlorate of potash, yields abundance of chloranile, a character in which it agrees with carbolic acid. Both substances also yield nitropicric acid when acted on by nitric acid, although in the case of creosote this acid is accompanied by others not yet examined. These results I have myself also obtained ; and it would appear, that if creosote be not carbolic acid, contaminated with some foreign matter, these two bodies are at least closely connected, and belong apparently to the same series, which is either that of benzoyle or that of phenyle. It is not improbable that creosote may be a definite compound of carbolic acid with some substance of closely allied composition, but of basic properties.

Creosote dissolves many organic substances, such as indigo, camphor, fats, essential oils, and resins, and undergoes numerous changes by the action of acids, alkalies, and other reagents, such as chlorine, potassium, and others. With oil of vitriol it is coloured purple, and appears to form a coupled acid. None of these reactions or products have been properly investigated, and we shall, therefore, not confuse the reader by a description of them, more especially as the composition of creosote itself is doubtful.

b. Picamar is the name given by Reichenbach to another oil discovered by him along with creosote in the heavy oil of tar. It is purified by a tedious process, with the aid of potash, with which it forms a crystalline compound. When pure, it is a colourless oil, of Sp. G. 1·10, of a burning and very bitter taste (hence its name from *pix* and *amarus*), and a slight smell. It boils at about 510°. It combines with alkalies, forming crystallisable salts, and may therefore be viewed as an acid in some sense, although it is quite neutral to test paper. Its composition is unknown.

c. Capnomor (from καπνος, smoke, and μοῖρα, part), is another oil, discovered by Reichenbach, in the heavy oil of tar, along with creosote and picamar. When the creosote is purified by solution in weak potash, the oil left undissolved contains a good deal of capnomor, which is purified by a tedious process. It is a limpid, colourless oil, of a high refracting power, with an aromatic odour of ginger, and a somewhat styptic after-taste. Its Sp. G. is 0·9775 ; it is quite neutral, and boils at 365°. With sulphuric acid it is coloured red, and yields a coupled acid. Nitric acid converts it into oxalic acid, nitropicric acid, and another crystalline substance not yet examined.

d. Eupion (from εύ, fine, and πιôν, oil or fat), is a fourth oily liquid, discovered by Reichenbach in oil of tar. Being more volatile than the rest, it is purified chiefly by rectification. When pure it is colourless, very fluid, not greasy to the feel, but less soft than water, tasteless, and of a somewhat agreeable odour, like that of some flowers, such as *narcissus*. Its Sp. G. is 0·740; and Reichenbach states that he has even obtained it so low as 0·633, being the lightest known liquid. It is volatile, boiling at 117° or lower. It is in the highest degree indifferent, resisting the action of the strongest acids and alkalies. In fact, as it is prepared from the oil of tar by rectification and the action of potash, sulphuric, and nitric acids alternately on the rectified oil, it is evident that it must resist these agents. There is good reason to believe that several, even many, different liquids have been described under this name, and that most of these are not ready formed in the tar, but products of the action of acids, &c., on the oil of tar. Reichenbach, however, by simple rectifications of the oil obtained by distilling rape oil, obtained a liquid having the characters of eupion. So much is certain, that similar liquids are formed by the action of oil of vitriol on oil of tar. The whole of the liquids called eupion are carbo-hydrogens, and their formula is either C H, or some multiple of this, or else one nearly approaching to such a multiple, as $C_5\ H_6$, &c. It is very remarkable that some of them are very volatile, while others, apparently of the same composition, require a strong heat, from 400° to 500° for example, to boil them.

The purest varieties of eupion burn with the aid of a wick, and yield a very brilliant luminous white flame, free from smoke, and may hereafter be turned to account.

3. Solid Products of the Distillation of Wood.

a Paraffine. This name is given (from *parum* and *affinis*, because its affinities are feeble) to a white solid volatile substance, very similar to wax, discovered by Reichenbach in tar. It occurs in the last portions of the rectification of the tar, which are semisolid. It is squeezed out, and purified by one or two crystallisations in ether, which dissolves it when boiling, and deposits it on cooling in beautiful silvery scales. These, when melted, assume, on cooling, the aspect of pure white wax.

Paraffine exists in large quantity in the Rangoon petroleum, and some other bituminous mineral products. It is formed in large quantity in the distillation of wax. It melts at 110°, and distils unchanged at a high temperature. Its Sp. G. is 0·870. It burns, in a wick, with a beautiful clear white light, free from smoke, fully equal to that of the finest wax, if not superior to it. Like eupion, it is highly indifferent, and it is, like eupion, a carbo-hydrogen, containing either CH, or some multiple of it, or a near approach to such a multiple. According to Lewy, it is $C_{20}H_{21}$. It is acted on by chlorine with the aid of heat, but the reaction is not yet studied. The strongest acids and alkalies do not act on it, even with the aid of heat, if we except fuming sulphuric acid.

b. Cedriret. This is another compound discovered by Reichenbach in oil of tar. When impure creosote is dissolved in potash, and acetic acid added, an oil separates, which contains the creosote and other oils; but a certain quantity of oily matter remains dissolved in the acetate of potash. This is distilled, until what passes over causes a red precipitate in a solution of sulphate of iron. It is then collected separately, being pure cedriret. It is a volatile solid, which crystallises in a solution of sulphate of iron, forming a net-work of orange-red crystals, which dissolve in oil of vitriol with a blue colour. Much of the colour of oil of tar is probably owing to this substance.

c. Pittacal. This is still another compound obtained by Reichenbach from the heavy oil of tar. When the heaviest portions are nearly neutralised by potash, the addition of barytic water gives rise to a deep-blue colour. This belongs to pittacal, but the mode of its purification is not yet published. When pure, it is a solid, like indigo, of a very fine deep-blue colour, exhibiting on the polished surface the aspect of gold. It admits of being fixed on cloth, and would make a valuable dye-stuff. Its composition is unknown, but it appears to contain nitrogen. Its name is derived from *πιττα*, pitch, and *καλλος*, beautiful. It is a compound of very great interest, although most probably a product of decomposition of the oil of tar, and not ready formed in it. It is very desirable that it should be further investigated.

d. Pyroxanthine. This is a volatile crystalline solid, first observed by Scanlan in the crude pyroligneous spirit. When this is rectified with lime, the lime becomes dark-brown; and when this coloured mass is acted on by hydrochloric acid, there is left undissolved a dark-brown matter, which is a mixture of pyroxanthine and a resinous matter. The mass is boiled with hot alcohol, which, on cooling, deposits the pyroxanthine in crystals, which are purified by recrystallisation. They are of an intense yellow colour, fusible, and volatile in a current of air, or with the vapour of other substances, but partly decomposed when heated alone in a dry tube. Pyroxanthine dissolves in sulphuric acid with a deep bluish-red, and in strong hydrochloric acid with a splendid purple colour, which soon passes to dark-brown. I found its composition to be very nearly $C_{21}\ H_9\ O_4$; but as it forms no definite compounds, I could not control the analysis.

Such are the chief products of the distillation of wood, as far as they are yet known. Their importance is very great, and will be still greater when they shall have been better studied, as most of them will admit of useful applications. But no doubt can be entertained that the above numerous list is far from being complete, and that more compounds remain to be discovered in tar. Indeed, there is even now good reason to believe that several or most of the substances characterising coal tar occur also, although in smaller quantity, in wood tar. Such substances are naphthaline, anthracene, and others. It is to be borne in mind that the composition of wood tar varies, according to the kind of wood, the presence or absence of oily or resinous substances, the comparative abundance of nitrogenised matter, and finally the temperature at which the distillation is carried on.

Wood coal, brown coal, or *lignite* yields, when distilled, an oil of the consistence of butter, in which creosote, paraffine, and probably eupion, are found, along with other products not yet examined.

PRODUCTS OF THE DISTILLATION OF COAL.

Coal differs from wood in several points, although it is unquestionably derived from the decay, under pressure, of woody fibre and the other substances which made up the mass of the early vegetation of which our coal-beds are the remains. Coal contains much less water, and a much larger per centage both of carbon and nitrogen, than wood. Hence it is decomposed at a higher temperature, and yields much ammonia, cyanogen, and other nitrogenised products. We shall not here dwell on ammonia and cyanogen, further than to mention that out of the aqueous products of the coal gas-works large quantities of ammonia are obtained; and that so much hydrocyanic acid is also present, that a patent was taken out some years since for the preparation of Prussian blue from the gas liquor. We proceed to describe the chief ingredients of coal tar.

a. Carbolic acid. Syn. *Hydrate of phenyle.* $C_{12}H_5O, HO$. This remarkable acid is found in that portion of the oil of coal tar which boils between 300° and 400°. This is agitated with twice its volume of potash ley, and the aqueous solution, on the addition of an acid, yields hydrated carbolic acid (impure) as a heavy oil. It is purified by rectification with a very little solid potash.

When pure, carbolic acid generally appears as an oily liquid, colourless, and of a high refracting power, neutral to test paper, of Sp. G. 1·062 to 1·065. It has a burning taste, and the odour of creosote, to which it has a very great resemblance. In certain circumstances it forms long needle-shaped crystals, which very readily lose the solid form by exposure to the atmosphere, and which also liquefy in sealed tubes, without any obvious cause. The crystals melt at 94°, and boil at 368°. The extraordinary resemblance between carbolic acid and creosote has been noticed above; and there can be little doubt that, if not essentially the same, they are closely connected and belong to the same series, or contain the same radical.

A splinter of pine-wood, if dipped, first in carbolic acid, and then in moderately strong nitric acid, becomes of a deep-blue, which soon passes into brown.

According to Laurent, carbolic acid is the hydrated oxide of phenyle, $C_{12}H_5$, and its formula is $(C_{12}H_5)\,O,\,HO$. This radical, phenyle, gives rise to a series of derived compounds which may be represented as follows :—

Hydrate of Phenyle, or Carbolic Acid .	$C_{12}\ H_5,O\ +HO$
Sulphocarbolic Acid (Sulphophenic Acid)	$C_{12}\ H_5\ O,\ HO+2\,SO_3$
Chlorophenesic Acid	$C_{12}\left\{\begin{matrix}H_3\\Cl_2\end{matrix}\right\}O,\,HO$
Chlorophenisic Acid, identical with the Chloridoptenic Acid of Erdmann	$C_{12}\left\{\begin{matrix}H_2\\Cl_3\end{matrix}\right\}O,\,HO$
Bromophenisic Acid	$C_{12}\left\{\begin{matrix}H_2\\Br_3\end{matrix}\right\}O,\,HO$
Nitrophenesic Acid . . .	$C_{12}\left\{\begin{matrix}H_3\\2\,NO_4\end{matrix}\right\}O,\,HO$
Nitrophenisic Acid, identical with Nitropicric Acid . .	$C_{12}\left\{\begin{matrix}H_2\\3\,NO_4\end{matrix}\right\}O,\,HO$

Thus the carbolic acid is connected with the derivatives of indigo, of salicyle, and other bodies, which yield nitropicric acid. This connection is also shown in the formation of chloranile, from carbolic acid, by the action of chlorate of potash and hydrochloric acid. (See under Indigo, the formation of chloranile from aniline). It is also shown, by the fact, that salicylic acid, $C_{14}H_6O_6$, when distilled alone, with lime, or with pounded glass, is resolved into carbonic acid, $2\,CO_2$, and carbolic acid, $C_{12}H_6O_2$. The action of carbolic acid, on organic compounds, is the same as that of creosote. Thus it dissolves indigo, &c. and coagulates albumen, preventing the putrefaction of animal substances.

With bases, it forms salts, some of which crystallise, but which retain an alkaline reaction. With oil of vitriol, it yields a coupled acid, sulpho-carbolic, or sulphophenic acid, which forms a soluble salt with baryta.

The formulæ in the above table illustrate the formation, by substitution, of the chlorophenesic and chlorophenisic, of the nitrophenesic and nitrophenisic acids. It is not necessary here to do more than point out their relation to carbolic acid and phenyle. The chlorobenzide of Mitscherlich, $C_{12}\ H_6\ Cl_6$ is, according to Laurent, hydrochlorate of chlorophenise, $3\ H\ Cl + C_{12}\left\{\begin{matrix}H_3\\ Cl_3\end{matrix}\right.$. This last body, chlorophenise, which is obtained by the action of potash on chlorobenzide, would appear to be derived by substitution, not from phenyle $C_{12}\ H_5$, but from benzole $C_{12}\ H_6$; although it may be derived also from oxide of phenyle $C_{12}\left\{\begin{matrix}H_5\\ O\end{matrix}\right.$; as may benzole itself. Chlorophenise cannot be obtained directly from hydrate of phenyle, or its derivatives; but, on the other hand, the series of benzole has an obvious relation to that of phenyle. In fact, Laurent considers benzole as in some measure the fundamental compound, or nucleus, and calls it phene $= C_{12}\ H_6$.

It has already been stated that nitrophenisic acid is identical with nitropicric acid. Nitrophenesic acid is somewhat similar, and forms salts which crystallise with facility, and detonate when heated. The nitrophenesate of baryta is a beautiful salt, like bichromate of potash.

b. Volatile Bases of Coal Tar.

Besides carbolic acid, Runge found in coal-tar two other acids, *rosolic* and *brunolic acids* (of which little is known), and three basic volatile oils, *kyanol*, *leukol*, and *pyrrol*. The last has been little examined; but the recent researches of Hoffmann have confirmed Runge's statements as to the first two, which have also been identified with bases produced from different quarters. They have, therefore, acquired a very high degree of interest.

1. *Kyanol*, $C_{12}\ H_7\ N$. Syn. *Aniline, Crystalline, Benzidam.* This very remarkable base has already been described as a product of the distillation of indigo with potash, and of anthranilic acid *per se*, under the name now generally adopted, of aniline. It has also been shown to be identical with the crystalline of Unverdorben, an oily base, extracted from animal oil of tar; and with benzidam, an oil formed by the action of sulphuretted hydrogen, or sulphuret of ammonium on nitrobenzide. Hoffmann has traced the production of aniline in various cases, as when

protonitrobenzoene, $C_{14}\left\{\begin{matrix}H_7\\NO_4\end{matrix}\right.$ is heated with lime. The reaction is as follows: $2\,CaO + C_{14}\,H_7\,NO_4 = 2\,(CaO,\ CO_2) + C_{14}\,H_7\,N$. In fact protonitrobenzoene being isomeric with anthranilic acid, it is not wonderful that both of them should be resolved into aniline and carbonic acid.

That there is a relation between aniline and carbolic acid appears from their formulæ; for aniline is the amidide of carbolic acid, or *phenamide*, being thus deduced from carbolate of ammonia. $C_{12}\,H_5\,O, NH_3 = HO + C_{12}\,H_5, NO_2$. The relation may be better exhibited thus:—

Carbolic Acid (anhydrous), or Oxide of Phenyle = $C_{12}\,H_5\,O$
Aniline, or phenylamide . . . . = $C_{12}\,H_5\,Ad$

As another experimental proof of this relation may be mentioned that salicylamide, $C_{14}\,H_5\,O_4,\ NH_2 = C_{14}\,H_7\,NO_4$, which has the same composition as protonitrobenzoene and anthranilic acid, both of which yield aniline, when heated with lime gives not aniline but carbolic acid, ammonia, and probably a carbo-hydrogen.

Aniline is recognised by striking a deep-violet-blue colour with chloride of lime (bleaching liquor), hence the name *kyanol*. It combines with acids, forming salts which crystallise with the utmost facility, hence the name *crystalline*. It is easily extracted from coal-tar oil, by agitating with hydrochloric acid, mixing the acid solution with an excess of milk of lime, and rectifying the basic oil which separates, and which is a mixture of aniline and of leukol. The former is the more volatile, and when the distilled liquid ceases to be coloured blue by chloride of lime, the leukol is coming over nearly pure, the aniline being found in the first distilled portions.

Aniline, when acted on by chlorine, yields trichloraniline (chlorindatmit of Erdmann) $C_{12}\left\{\begin{matrix}H_4\\Cl_3\end{matrix}\right\}N$ along with chlorophenusic acid $C_{12}\left\{\begin{matrix}H\\Cl_4\end{matrix}\right\}O,\ HO$. With chlorate of potash, and hydrochloric acid, it yields chloranile, $C_{12}\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right.$. With bromine it yields tribromaniline $C_{12}\left\{\begin{matrix}H_4\\Br_3\end{matrix}\right\}N$ (bromaniloide of Fritzsche. Strong nitric acid first colours aniline blue, and then yellow, with a violent reaction, the result of which is the conversion of aniline into nitropicric acid.

2. *Leukol*, or *Quinoleine?* $C_{18}\,H_8\,N$ (Hoffmann), or $C_{18}\,H_7\,N$

(Laurent, Gerhardt), is prepared as above. Its properties have been formerly mentioned, although under a different name; for the most recent researches tend to the conclusion, that it is identical with quinoleine, the oily base obtained by the action of heat, aided by potash, on cinchonine, quinine, strychnine, and probably other bases. This identification is very curious, like that of aniline and kyanol, and the occurrence of quinoleine in coal-tar is a very remarkable fact. The formula here given for quinoleine differs from that given under that head, which is $C_{19} H_8 N$. As, however, there may still be some doubt as to the identity of leukol and quinoleine, I shall not alter the formula first given for quinoleine, until further experiments have decided the exact composition of that base, and have also fixed that of leukol.

Of *pyrrol*, and of *rosolic and brunolic acids*, so little is known that we need not dwell on them.

c. Volatile Carbo-hydrogens in Coal Tar.

a. Naphthaline, $C_{10} H_4$, or $C_{20} H_8$. This remarkable compound occurs in all kinds of tar, but most abundantly in coal-tar, as being formed at a very high temperature. It is formed in additional quantity when any of the elements of oil of tar, such as creosote, carbolic acid, &c., or even alcohol and ether, are passed through tubes heated to a strong red-heat. It is easily obtained by re-distilling coal-tar, when the latter portions are so full of naphthaline as to be semisolid. It is well squeezed out, and purified by sublimation and crystallisation in hot alcohol. Or the oil of coal-tar is saturated with chlorine gas, which, by destroying some of the oils, allows the naphthaline to crystallise.

Pure naphthaline is colourless and volatile, and forms large tabular, transparent crystals, of a very peculiar smell, and an acrid aromatic taste. It boils at 414°, but distils easily with the vapours of water, and is dissipated, like camphor, if left exposed at the ordinary temperature.

It is acted on by chlorine and bromine, which combine with it in the first instance, and also give rise to a large number of compounds formed by substitution; and by sulphuric and nitric acids, each of which produces a number of new compounds with it. These changes have been studied with singular perseverance and remarkable sagacity, by Laurent, more especially the action of chlorine, bromine, and nitric acid. His researches have been attended with unusual success, and he may be said to have originated and established, by these researches, the now received doctrine of substitutions. I cannot hope to give even an accurate outline of all that Laurent has done in this department, because I have nowhere seen a complete account of these curious results as they now stand; but until the author himself shall publish a complete account of his researches on naphthaline, I shall place before the reader such a general account of them as shall show the great importance of the subject, and some of the interesting facts already ascertained.

1. Action of Chlorine and Bromine on Naphthaline.

(It is necessary here to explain the principle of nomenclature, provisionally adopted by Laurent, especially for cases like this of substitutions, where the ordinary nomenclature is entirely inapplicable. The nomenclature of Laurent may be thought, by some, uncouth; but it is simple, systematic, and consistent with itself. Beginning with naphthaline, he gives to the compounds formed by the successive substitution of chlorine for hydrogen, names beginning with *chlo,* and ending with a syllable in which the vowels a, e, i, o, and u, are employed to designate the replacement of 1, 2, 3, 4, and 5 eq. of hydrogen. Thus, if, in naphthaline, $C_{20}H_8$, 1 eq. of hydrogen is replaced by chlorine, we have the compound $C_{20}\left\{\begin{matrix}H_7\\Cl\end{matrix}\right.$. This is called chlonaph*tase.* The compound $C_{20}\left\{\begin{matrix}H_6\\Cl_2\end{matrix}\right.$ is chlonaph*tese;* $C_{20}\left\{\begin{matrix}H_5\\Cl_3\end{matrix}\right.$ is chlonaph*tise,* &c. The corresponding compounds of bromine are bronaph*tase,* bronaph*tese,* and bronaph*tise.* When we get as far as chlonaph*tuse* $C_{20}\left\{\begin{matrix}H_3\\Cl_5\end{matrix}\right.$ as there are no more vowels, we begin again with *a,* adding a syllable to the word. Thus, $C_{20}\left\{\begin{matrix}H_2\\Cl_6\end{matrix}\right.$ is chlonaph*talase,* $C_{20}\left\{\begin{matrix}H\\Cl_7\end{matrix}\right.$ is chlonaph*talese,* and $C_{20}Cl_8$ is chlonaph*talise,* and so on with bromine. When hydrogen is replaced, partly by chlorine, partly by bromine, then the name is so constructed that the final syllable indicates the sum of the equivalents of chlorine and bromine, while both chlorine and bromine are prefixed. Thus, chlonaphtose is $C_{20}\left\{\begin{matrix}H_4\\Cl_4\end{matrix}\right.$; and the compound $C_{20}\left\{\begin{matrix}H_4\\Cl_3\\Br\end{matrix}\right.$ is chlor*i*bronaph*tose*; $C_{20}\left\{\begin{matrix}H_4\\Cl\\Br_3\end{matrix}\right.$ is chlor*a*bronaph*tose.* The former of these two may also be brom*a*chlonaph*tose,* and the latter brom*i*chlonaph*tose.* We shall see, hereafter, that it may be necessary to use both forms to distinguish different compounds which are isomeric. Again, where hydrogen is replaced by NO_4, we have, ($NO_4 = X$), $C_{20}\left\{\begin{matrix}H_7\\X\end{matrix}\right.$ nitronaphtalase, and so forth. It is evident that this nomenclature, although it gives rise to words of a singular aspect, is yet easily understood, and may even, in many cases, serve as well as a formula to remind us of the composition. Laurent has applied it to many other series, as we have seen in the series of phenyle, where we have chlorophenesic, chlorophenisic, and chlorophenusic acids, &c.)

When chlorine is brought in contact with naphthaline, the latter melts, and there are formed at once two compounds of chlorine and naphthaline; the chloride of naphthaline, $C_{20}H_8 + Cl_4$; and the subchloride of naphthaline $C_{20}H_8 + Cl_2$. At the same time hydrochloric acid is disengaged, arising from the action of chlorine on one of these chlorides. The former is a solid, which is best purified by solution in hot oil of petroleum, which deposits it on cooling in crystals. It may also be purified by means of boiling ether, which dissolves it to a certain extent, and deposits it on cooling. Chloride of N. is decomposed by heat, yielding no less than four different isomeric forms of chlonaphtese. An alcoholic solution of potash converts it into two more forms of chlonaphtese. It is also acted on by chlorine, bromine, nitric acid, and sulphuret of ammonium, yielding many new compounds.

Subchloride of N. is an oily liquid, which by the action of heat is partially changed into hydrochloric acid, and one form of chlonaphtase. An alcoholic solution of potash also converts it into chlonaphtase and chloride of potassium. Chlorine converts it into two chlorides of chlonaphtase, isomeric but distinct; if the heat is too strong there is formed one kind of chlonaphtise.

When bromine is made to act on naphthaline, no bromide of N. is formed, but hydrobromic acid is separated and bronaphtase is produced.

Chlonaphtase, $C_{20}(H_7Cl)$ is obtained by acting on subchloride of N. by alcoholic solution of potash. On the addition of water, an oily liquid separates, which is purified by rectification, and is then chlonaphtase. No isomeric modification of it is yet known, but the existence of such is extremely probable. Bromine acts on it, converting it into bromide of chlorabronaphtese, $Br_4 + C_{20}H_6ClBr$.

Bronaphtase, $C_{20}(H_7Br)$ is formed by the direct action of bromine on naphthaline, care being taken to avoid excess of bromine, which would form bronaphtese, and excess of naphthaline which would remain unchanged. Bronaphtase is a colourless oil, decomposed by chlorine and bromine, the latter converting it into bronaphtese and the products of the further action of Bromine on bronaphtese. As yet only one form of bronaphtase is known.

Chlonaphtese, C_{20} $(H_6 Cl_2)$, occurs in no less than 7 different isomeric forms. These are distinguished by Laurent as modifications *a*, *c*, *ad*, *e*, *f*, *x*, and *y*, but I am not aware of the principle on which these letters are selected. *a*, *c*, *f*, and *x*, are obtained by the action of heat on the chloride of N.; *ad* and *e* by boiling chloride of N. with tincture of potash; and *y* by the action of chlorine on nitronaphtese. *a* and *x* are liquid, all the rest crystallise easily. The solid forms have each a different point of fusion, and the whole 7 give different results when acted on by chlorine and bromine. Since, therefore, the composition of all 7 is the same, we are compelled to adopt the conclusion that it is not the same 2 eq. of hydrogen which are replaced by chlorine, and that it is not indifferent which equivalents of hydrogen are thus replaced, but that, on the contrary, the properties of these compounds depend on the particular equivalents or molecules of hydrogen replaced by chlorine, and that consequently the arrangement, or relative as well as absolute position of these molecules in the compound molecule, is a matter of far greater importance, in reference to chemical characters, than the properties of the elements, or their place in the electro-chemical arrangement.

Referring to what I have said on the subject of types, at pp. 252-253, I would here point out that naphthaline is a type, the molecule of which is made up of 20 equivalents (not single atoms, but molecules) of carbon, and 8 equivalent molecules of hydrogen; and that chlonaphtese is a sub-type, in which the 20 molecules of carbon are associated, as in the fundamental type, with 8 other molecules, not all, as before, of hydrogen, but 6 of hydrogen and 2 of chlorine, a body usually considered as entirely opposed to hydrogen, chlorine being strongly negative, and hydrogen strongly positive. Yet the type remains unchanged, and we cannot help seeing that the 2 molecules of chlorine, *in virtue of their position in reference to the* 20 *of carbon*, are playing the part of 2 molecules of hydrogen.

Further, if we conceive the 8 molecules of hydrogen in the fundamental type to occupy each a fixed position, in relation to the 20 of carbon, we see from the wonderful phenomena just indicated, from the existence of 7 distinct forms of chlonaphtese, that, in each of these, a different pair of molecules of hydrogen has been replaced by chlorine. If the 8 molecules of hydrogen be supposed to be numbered, according to the fixed position of each in the compound molecule of the type, then we can see that in chlonaphtese *a*, the molecules 1 and 2 may be those replaced, while in *c* the molecules 6 and 7 may be those replaced by chlorine, and so on. It is easy to calculate that in this way at least 28 different isomeric forms of chlonaphtese may exist, and of these 7 are already known.

Our space will not admit of details on the different forms of chlonaphtese, but I have thought it indispensable to explain the view now taken of these singular compounds, in a general way. It is evident that we may expect much light to be thrown on the obscure subject of the molecular arrangement of compounds by continued researches in the same direction. The recent progress of those departments of physics which are most closely allied to chemistry, has established the existence of certain relations between the atomic weight and constitution of compounds and their physical properties, such as volume or density, volatility, state in regard to cohesion, solidity, fluidity, &c., and crystalline form. We now see a prospect of tracing the connection between the molecular arrangement of compound bodies and their chemical properties; and we may even hope hereafter to be enabled, simply by accurate observation of the external properties of a body, physical and chemical, to ascertain its composition and constitution; and also to predict with accuracy the properties of compounds yet unformed, the formation of which will probably become a problem, solvable by a few rules of universal application.

For the present, we have only the distant prospect of these results; but we have only assiduously to pursue the study of nature on true inductive principles, in order to be hereafter enabled to bring into order the chaos, so to speak, of interesting and important observations, the number of which is hourly increasing, while a large proportion of them have not yet found a use or an application. We must now return to the derivatives of napththaline, which we have only space briefly to name.

Bronaphtese, $C_{20}\,(H_6\,Br_2)$, is easily formed by the action of bromine on napththaline or on bronaphtase. It is a crystallisable solid, and probably corresponds to chlonaphtese, *c*. Only one bronaphtese is yet known. It forms several compounds with bromine.

Chlonaphtise, $C_{20}\,(H_5\,Cl_3)$ occurs in 6 different forms (out of 55 which are possible), *a*, *ac*, *c*, *g*, *d*, and *ad*, all of which are crystallisable solids. They are obtained in different ways: *a* by boiling with tincture of potash the oily modification of chloride of chlonaphtase; *ac* by the action of chlorine on chlonaphtese *ad*, melted; *c* and *g*, along with some of *a*, by boiling with tincture of potash the crystallised chloride of chlonaphtase; *d* by distilling the crystallised chloride of chlonaphtase; and *ad* by boiling with tincture of potash the double chloride of naphthaline and of chlonaphtase; *a* is converted by chlorine into chlonaphtose *a*; and bromine converts it into chloribronaphtose *a*.

Bronaphtise C_{20} (H_5 Cl_3) is obtained by heating the bromide of bronaphtise, when bromine is given off. It is crystallisable. Only one form is yet known.

Chlonaphtose C_{20} (H_4 Cl_4) occurs in 4 isomeric forms, *a*, *b*, *e*, and *k*, out of a very large number which are possible. They are all crystallisable. It is unnecessary to mention the methods employed to obtain them, which are analogous to those already described for chlonaphtise or chlonaphtese.

Bronaphtose, C_{20} (H_4 Br_4) appears to exist in two forms, *a* and *b*, both crystallisable.

Chlonaphtuse, C_{20} (H_3 Cl_5) and *Bronaphtuse*, C_{20} (H_3 Br_5), are not yet known.

Chlonaphtalase, C_{20} (H_2 Cl_6) is obtained by the action of chlorine on chlonaphtise *a*. It forms soft flexible prisms.

Chlonaphtalese, C_{20} (H Cl_7) is not yet known.

Chlonaphtalise, C_{20} Cl_8, the compound in which all the hydrogen of naphthaline is replaced by chlorine, is obtained by continuing the action of chlorine on chlonaphtise *a*. It is also crystallisable. Laurent, apparently from its crystalline form, considers it to correspond with the modifications *c* of chlonaphtese and chlonaphtise; and for the same reason he considers the only chlonaphtalase known, as chlonaphtalase *a*. In the case of chlonaphtalise, if different modifications can occur, they must depend on a different principle from that which regulates the modifications of those compounds in which both chlorine and hydrogen are concerned. But until Laurent shall publish a complete account of his views, it is not easy to ascertain exactly what those views are. I suspect some error in the only account of these researches to which I could refer.

Besides the above, there are a number of compounds derived from naphthaline, in which the hydrogen is replaced by bromine and chlorine at once.

Chlorebronaphtise a, C_{20} (H_5 Cl_2 Br) is a crystalline solid very similar to chlonaphtise *a*.

Chlorebronaphtose b, C_{20} (H_4 Cl_2 Br_2) is obtained by the action of bromine on chlonaphtese *f*.

Chloribronaphtose a, *Bromachlonaphtose a*, and *Bromachlonaphtose b* are three isomeric compounds. The first is obtained by the action of bromine on chlonaphtise *a*, and the bromine is, therefore, placed second in the name. The two others are both formed when chlorine acts on bronaphtese. These are the compounds alluded to at p. 253. They furnish a very beautiful proof of the truth that the position of the replaced or replacing molecule is all-important. They are all crystallisable.

Bromechlonaphtose b, $C_{20}(H_3 Cl_3 Br_2)$ is a crystalline solid, obtained by boiling chloride of bromechlonaphtise with tincture of potash.

Chloribronaphtuse, $C_{20}(H_3 Cl_3 Br_2)$ is a crystalline solid, formed by the action of bromine on chloride of naphthaline.

There remain to be described some compounds, analogous to the chlorides of naphthaline, and containing consequently chlorine or bromine, in addition to the type or subtype.

Chloride of chlonaphtase $Cl_4 + C_{20}(H_7 Cl)$, is obtained by the action of chlorine on the subchloride of naphthaline. It is the most remarkable of the whole series from the great size and beauty of its crystals. It occurs in an isomeric form as an oily liquid. When distilled, these compounds yield different forms of chlonaphtise mixed together.

Chloride of chlonaphtese, $Cl_4 + C_{20}(H_6 Cl_2)$ occurs in three isomeric forms. *a* and *x* are oily liquids, derived respectively from chlonaphtese *a* and *x* by the action of chlorine. *c* is derived from chlonaphtese *c* in the same way, and is crystalline. They all yield chlonaphtose when heated, but in different forms.

Bromide of chlonaphtese, $Br_4 + C_{20}(H_6 Cl_2)$ is obtained by the action of bromine on chlonaphtese *c*. It is crystalline. An excess of bromine produces at least five different compounds.

Bromide of chlorabronaphtese, $Br_4 + C_{20}(H_6 Br Cl)$, is formed when bromine acts on chlonaphtase. It is crystalline.

Bromide of bronaphtese, $Br_4 + C_{20}(H_6 Br_2)$ is formed by the action of bromine on bronaphtese. It is crystalline, and when distilled yields hydrobromic acid and bronaphtose.

Subbromide of bronaphtise, $Br_2 + C_{20}(H_5 Br_3)$ is formed along with the preceding. It is also crystalline.

Bromide of bronaphtise, $Br_4 + C_{20}(H_5 Br_3)$ is also a highly crystalline solid.

Subchloride of bronaphtase, $Cl_2 + C_{20}(H_7 Br)$, formed by the action of chlorine on bronaph.ase, crystallises in regular rhomboidal plates.

Chloride of bronaphtese, $Cl_4 + C_{20}(H_6 Br_2)$ crystallises in long prisms. *Perchloride of bronaphtise*, $Cl_5 + C_{20}(H_5 Br_2)$ crystallises in right prisms with rhombic base.

Chloride of bromechlonaphtise, $Cl_4 + C_{20}(H_5 Br_2 Cl)$ crystallises in oblique rhombic prisms. When boiled with tincture of potash it yields *bromechlonaphtuse*, $C_{20}(H_3 Br_2 Cl_3)$.

All the preceding compounds have been discovered, studied, analysed, and described by Laurent, besides a large additional number of derivatives of naphthaline, under the agency of chlorine and bromine, which he has not so fully examined. Those here named are sufficient to illustrate the endless variety of compounds attainable. Every subtype of the original type of naphthaline admits of numerous permutations, and where both chlorine and bromine are present, the number of possible permutations is enormously increased. In short, these remarkable researches have only made us acquainted with a very small selection of the possible products of the action of chlorine and bromine on naphthaline, *the type remaining unchanged.*

Thus the subtype chlonaphtose C_{20} $(H_4 Cl_4)$, admits of 65 isomeric modifications, all different, as does of course bronaphtose also. But these subtypes may yield the modified subtypes, chlorabronaphtose, chlorebronaphtose, chloribronaphtose, bromachlonaphtose, bromechlonaphtose, and bromichlonaphtose, and others, difficult to name, depending on the relative proportions and positions, in the molecule of the subtype, of the 4 eq. chlorine and bromine. It is easy to imagine 14 such modified subtypes, and there appears no reason why each of them, with the two subtypes, should not admit of at least 65 isomeric forms. This would give 1040 isomeric forms, all included under the two subtypes chlonaphtose and bronaphtose, or under one subtype which may be called *naphtose,* C_{20} $(H_4 X_4)$. X is here put for chlorine or bromine.

2. Action of Sulphuric Acid on Naphthaline.

When naphthaline is dissolved in warm oil of vitriol to saturation, the solution, if left exposed to the air, becomes a semisolid mass of a dirty purplish colour. This, dried on a porous brick, leaves a quantity of scales, very soluble in water and alcohol, which are a mixture of two acids.

a. Hyposulphonaphthalic acid, $C_{20} H_8, S_2 O_5 + HO$? The above mixture, being dissolved in water, is saturated with carbonate of lead, which forms insoluble sulphate of lead, and two soluble salts, one of which is soluble in alcohol and contains this acid, and yields it when decomposed by sulphuretted hydrogen. The acid forms a hard crystalline fusible mass of an acid and bitter taste. Its salts are soluble and crystallisable. Their formula is $C_{20} H_{16} S_2 O_5, MO$.

b. Hyposulphonaphtic acid, $C_{11} H_5 S_2 O_6 = C_{11} H_4 S_2 O_5, HO$? The lead salt insoluble in alcohol contains this acid, the salts of which are soluble, bitter, and hardly crystallisable. It is probable that a third acid accompanies these two: for Faraday obtained a third salt of baryta and Berzelius found a third salt of lead in the mother liquid of the other two. Faraday's salt, which remains with the sulphate of baryta formed in the process by the free sulphuric acid, and may be extracted by boiling water, yields about 42 per cent. of sulphate of baryta when calcined.

The vapours of anhydrous sulphuric acid, passed over fused naphthaline, form with it a red liquid. If the acid be in excess, there is formed a new acid, the *hyposulphoglutinic acid,* besides small quantities of the preceding acids; if there be excess of naphthaline there are formed two neutral bodies, *sulphonaphthaline* and *sulphonaphthalide.*

Hyposulphoglutinic acid, when pure and dry, is a hard glassy mass. When precipitated from its salts by stronger acids, it forms a viscid hydrate like turpentine. Its salts are generally soluble and do not crystallise. Its composition is unknown.

Sulphonaphthaline $C_{20} H_8 S O_2$? is a crystalline fusible solid.

Sulphonaphthalide, $C_{24} H_{10} S O_2$? is a crystalline powder not fusible at 212°.

3. Action of Nitric Acid on Naphthaline, and its Derivatives.

Nitric acid acts on naphthaline, and gives rise to a whole series of compounds in which $N O_4$ is substituted for hydrogen. The same principles apply here as in the action of chlorine and bromine on naphthaline. It is to Laurent that we are indebted for our knowledge of these compounds, which our space will only allow us to name.

Nitronaphtalase, $C_{20} H_7 X$, (X is here put for $N O_4$), is best formed by causing nitrous acid to pass through melted naphthaline. It is purified by means of alcohol, and forms long prisms of a sulphur-yellow colour, fusible at 110°. Chlorine decomposes it, producing chlonaphtose. Nitric acid converts it into *nitronaphtalese.*

Nitronaphtalese, $C_{20} (H_6 X_2)$, forms a crystalline powder fusible at 365°, insoluble in water, very sparingly soluble in alcohol.

Naphtalase, $C_{20} (H_7 O)$ is a yellow crystalline solid formed by gently heating nitronaphtalase with 10 parts of lime slightly moistened. It communicates to oil of vitriol a magnificent blue colour. It is insoluble in alcohol as well as in water, otherwise it would recal pyroxanthine, which is yellow and volatile and colours sulphuric acid purple.

Nitronaphtaleise, $C_{20} (H_{5\frac{1}{2}} X_{2\frac{1}{2}})$? is a crystalline compound formed when naphthaline is added in small quantities to a large mass of hot nitric acid. Nitronaphtalese is produced along with it. It is pale-yellow and very fusible, becoming liquid even in boiling alcohol. This great fusibility prevents us, notwithstanding its strange formula, from considering it as a mixture of nitronaphtalese and nitronaphtalise, the former of which melts at 365°, the latter at 410°, and which are very insoluble in ether, in which liquid nitronaphtaleise readily dissolves.

Nitronaphtalise, $C_{20}(H_5 X_3)$ is formed along with the preceding, and crystallises in rhomboidal plates of a pale-yellow colour, fusible at 410°.

Nitronaphtale, $C_{19} H_5 N_3 O_{11}$, is a crystalline substance, formed by the long-continued action of nitric acid on the mother liquor of all the preceding. It melts at 420°, and sometimes solidifies in an amorphous state ; a slight heat, or touching the melted substance with a point, causes it to crystallise.

Nitronaphtalesic acid, $C_{16} H_{4\frac{1}{2}} N_{1\frac{1}{2}} O_4$? $C_{32} H_9 N_3 O_8$? This acid is formed when nitronaphtalese is boiled with tincture of potash, and is separated from the potash by nitric acid. When dry it is brownish-black, and forms brown salts, which are soluble and uncrystallisable. *Nitronaphtaléisic acid,* $C_{12} H_4 O_6 N_{1\frac{1}{2}}$, or $C_{24} H_8 O_{12} N_3$, is a similar acid, formed from nitronaphtaléise. *Nitronaphtalisic acid* is another brown acid, formed in the same way from nitronaphtalise.

Oxide of chloroxénaphtose, $O_2 + C_{20}(H_4 Cl_2 O_2)$, is formed when nitric acid acts on crystallised chloride of chlonaphtose. It appears as a yellow crystalline solid. It is accompanied by chloranaphtisic acid, into which it is also converted by boiling with tincture of potash.

Chloranaphtisic acid, $C_{20} H_5 Cl O_6$, is formed from the preceding compound, as follows : $C_{20} H_4 Cl_2 O_4 + HO + 2KO = KCl + (C_{20} H_5 Cl O_6 + KO)$. It is separated from the potash by adding an acid, and forms yellow crystals, fusible at 392°. Its salts are for the most part insoluble, and exhibit the most beautiful colours, including yellow, orange, red, and carmine.

Oxide of chloroxenaphtalise, $O_2 + C_{20} Cl_6 O_2$, is obtained along with chlophtalisic acid and other compounds, when nitric acid is boiled with *chlonaphtalase,* $C_{20} H_2 Cl_6$. It forms golden scales.

Chloroxénaphtalesic acid, $C_{20} H Cl_5 O_6$, is formed when the preceding compound is acted on by potash, which at once changes it into a fine carmine-red substance, from which acids separate the new acid as a yellow crystalline powder. It forms beautiful red salts with potash and ammonia. It is formed as follows : $C_{20} Cl_6 O_4 + HO + 2KO = (C_{20} H Cl_5 O_6 + KO) + KCl$.

Phtalic or naphtalic acid, $C_{16} H_4 O_6, 2HO = C_{16} H_6 O_8$, is formed by the action of nitric acid on chloride of naphthaline. It forms rounded groups of lamellar crystals, and yields crystallisable salts. When distilled with lime, it yields benzole (phéne), and carbonic acid, $C_{16}H_6O_8 = 4\,CO_2 + C_{12}H_6$. When the hydrated acid is distilled, it yields the anhydrous acid in fine elastic needles.

The acid phtalate of ammonia, $C_{16}H_4O_6, NH_4O, HO$, when heated yields water, 4 HO, and *phtalimide*, $C_{16}H_5NO_4$.

Phtalamide, $C_{16}H_6NO_5$, is obtained by acting on anhydrous phtalic acid by ammonia. It appears that phtalimide is acid phtalate of ammonia, minus 4 eq. water, while phtalamide is anhydrous phtalate of ammonia, $C_{16}H_4O_6 + NH_3$, minus 1 eq. water. Both are crystalline solids, and both appear to form definite compounds with oxide of silver.

Nitrophtalic acid, $C_{16}H_3NO_{10}$, 2 HO, is derived from phtalic acid by the substitution of 1 eq. NO_4 for 1 eq. hydrogen. $C_{16}H_4O_6 - H + NO_4 = C_{16}H_3NO_{10}$. It forms beautiful pale-yellow crystals; and when gently heated, it yields the anhydrous acid in fine white needles.

Chlophtalisic acid, $C_{16}HCl_3O_6$, is formed along with the oxide of chloroxenaphtose when chlonaphtalase is boiled with nitric acid. It is crystallisable, and represents anhydrous phtalic acid, in which 3 eq. hydrogen have been replaced by 3 eq. chlorine.

4. Action of Sulphuretted Hydrogen on the Nitrogenised Compounds derived from Naphthaline.

Naphtalidam, $C_{20}H_9N$. This is a very interesting base, formed by the action of sulphuretted hydrogen, aided by ammonia, on an alcoholic solution of nitronaphtalase. It may be obtained, although more slowly, without the use of ammonia. The mixture becomes of a dirty green, and the addition of sulphuric acid causes the solution to become thick from the separation of sulphate of naphtalidam. This salt is purified, and decomposed by ammonia, when the liquid is soon filled with fine white needles of pure naphtalidam. It is a very powerful base, melting at 86°, and boiling at 582°. When distilled, it is apt to continue liquid till cooled to 32°. The liquid base, if exposed to the air, absorbs oxygen, and becomes of a dirty violet colour. It forms white crystallisable salts with all the acids, and its hydrochlorate forms double salts with the bichlorides of platinum and mercury.

The discovery of this base, and of the ingenious method by which it is formed, is due to Zinin, who has also found that the other nitrogenised derivatives of naphthaline, treated in the same way, form similar bases. That from nitronaphtalese is crystallisable, and forms a hydrochlorate in scales.

The formation of these bases throws great light on the true nature of the vegetable alkalies. Zinin obtained from nitrobenzide, by the same method, a base, an oil which he called benzidam ; but Hofmann has shown its identity with aniline.

To judge from the action of chlorine unaided by heat, and of nitric acid, on naphthaline, that body, $C_{20}H_8$, is composed of two carbo-hydrogens, $C_{16}H_4$ and C_4H_4, the latter of which is more easily altered. The former, plus 6 eq. oxygen, yields phtalic acid, $C_{16}H_4 + O_6$; and the substitution in phtalic acid of NO_4 (= X), for H yields nitrophtalic acid, $C_{16}\left\{\begin{matrix}H_3\\X\end{matrix}\right. + O_6$.

β. *Anthracene*, $C_{30}H_{12}$. This compound, which is isomeric with naphthaline, is also found in coal-tar, and is sometimes called paranaphthaline. It melts at 356°, and distils at 392°, yielding foliated plates. When acted on by nitric acid, it gives rise to a series of compounds, in which oxygen is substituted for hydrogen, while the compounds thus formed combine with hyponitrous acid. Thus, we have

Anthracene	$C_{30}H_{12}$
Hyponitrite of Anthracenase	$C_{30}H_{11}O + NO_3$
Bi-hyponitrite of Anthracenese	$C_{30}H_{10}O_2 + 2NO_3$
Ter-hyponitrite of Anthracenise	$C_{30}H_9O_3 + 3NO_3 + 3HO$
Hyponitrite of Anthracenose	$C_{30}H_8O_4 + NO_3$
Hyponitrite of Anthracenuse	$C_{30}H_7O_5 + NO_3 + HO$
Anthracenuse	$C_{30}H_7O_5$
Chloranthracenese	$C_{30}H_{10}Cl_2$

The second compound of the above list is not known ; but its existence is probable. In all the works to which I have access, there appear to be errors, probably of the press, in the table, which I have ventured to correct, so as to bring the formulæ into correspondence with the systematic names devised by Laurent, who discovered all these substances, on the same principle as in the case of naphthaline.

γ. *Chrysene*, C_3H or $C_{12}H_4$ is found among the last portions of the rectification of coal-tar. It is a yellow crystalline solid, insoluble in most liquids. It melts at 455°.

δ. *Pyrene*, $C_{10}H_2$ or $C_{15}H_3$ is found accompanying the preceding. It is a good deal more fusible. When acted on by nitric acid both of the above compounds yield modifications, called, by Laurent, the hyponitrites of chrysenase and of pyrenase, $C_{12}H_3O + NO_3$ and $C_{15}H_2O + NO_3$. The former, by the continued action of nitric acid, is converted into $C_{24}H_5O_3 + 2NO_3$, which Laurent calls *nitrite of chrysenese* (properly, of *chrysenaese ?*)

When bituminous shale is distilled, it yields a thick empyreumatic oil, composed of several products. Among these is an oil apparently identical with eupion, and another very peculiar oil, called *ampeline.* This oil has neither taste nor smell, but is in some points more analogous to creosote than to any other substance. It dissolves in water, but a few drops of acid cause it to separate. Its composition is still unknown. It may possibly be a product of the action of oil of vitriol, which is used in its preparation, on some other substance.

Ampelic Acid is formed by the action of nitric acid on that part of the oil of schist which distils at 300°. It is oily, soluble in hot water, and forms very soluble salts. Its composition is not known with certainty. A similar oil, obtained from coal-tar, was found to contain $C_{14} H_6 O_6$. This would be isomeric with hydrated salicylic acid.

FOSSIL RESINS, WAX, OIL, NAPHTHA, &c.

Retinite or *Retinasphalt,* is a fossil resin found in lignite or wood-coal. It is fusible and combustible, and almost entirely soluble in alcohol. *Retinic acid,* $C_{21} H_9 O_3$, was found by Johnston in the retinasphalt of Bovey.

Hatchetine is another fossil resin found in the lignites of Wales. It is colourless, or slightly yellow, fusible and volatile.

Scheererite is a colourless, translucent substance, of a pearly lustre, found in the Swiss lignites. Both Hatchetine and Scheererite appear to be carbo-hydrogens, and much resemble paraffine, not quite pure.

Middletonite is a fossil resin, found, near Leeds, in coal.

Idrialine is a remarkable solid carbo-hydrogen, found in the quicksilver-mines of Idria. Its composition is C_3 H, or perhaps $C_{21} H_7$; it colours oil of vitriol intensely blue, forming a coupled acid. *Succisterene,* a solid body obtained by Pelletier and Walter in the distillation of amber, has the same composition, and colours sulphuric acid blue. It is, therefore, in all probability, identical with idrialine.

Ozokerite or *Fossil Wax* is found in large masses in the bituminous schist of Slamick in Moldavia. When distilled, it yields a substance like wax, and also a good deal of paraffine. Ozokerite is very fusible, and burns with a bright flame.

Fichtelite is a fusible, volatile, crystallisable solid, found in branches of pine-trees, in the peat of the turbaries in the Fichtelgebirge. It appears to have the formula $C_{20} H_{15}$, and is probably derived from essence of turpentine, $C_{20} H_{16}$.

Tekoretine, Phylloretine, Xyloretine, and *Boloretine,* are the names of four resinous compounds, found in the peat of Denmark, on the remains of pine-trees. Tekoretine and Phylloretine are both fusible, volatile, and crystallisable. The former appears to be $C_{10}H_9$, the latter C_5H_3. Xyloretine is less fusible, and is decomposed by heat. It crystallises, and its formula is said to be $C_{40}H_{33}O_4$, which only differs from that of sylvic acid by 1 eq. hydrogen. Boloretine is fusible, but does not crystallise. Its formula is $C_{40}H_{32} + 3\,HO$, but it occurs also with 5 and 6 eq. of water.

Asphaltum, Mineral Pitch, Pitch of Judea. These are the names of certain substances of similar characters, found in different parts of the world, as in Trinidad, in Hanover, and at the Dead Sea in Palestine. They all resemble pitch in aspect, and are composed of a dark-brown resin, mixed with more or less of a brilliant black matter, *asphaltene*, $C_{20}H_{16}O_3$, or of a liquid volatile oil, *petrolene*, $C_{20}H_{16}$. The former of these is probably an oxide of the latter. The different kinds of asphaltum are much used for waterproof cements, and for pavements, or roofs. *Naphteine* is a somewhat analogous substance, found in the limestones of the Maine et Loire.

Petroleum and *Naphtha.* In certain spots, in the neighbourhood of the Caspian, in Ava, at the Tegernsee in Bavaria, at Amiano in Italy, and near Neufchatel, as well as in other places, pits dug in the earth become filled with water, on which floats, more or less abundantly, an oily matter, formerly called rock-oil. The purer kinds are little coloured and very fluid, and when distilled with water leave hardly any residue. These are called naphtha. Other kinds, as the petroleum of Rangoon in Ava, are dark-coloured and semisolid, but become liquid at 80° or 90°. These yield by distillation, first, much naphtha, nearly colourless, and then much paraffine, which is easily purified. Naphtha, when pure, has the Sp. G. 0·755, and its formula is C_6H_5. Rectified naphtha is used for the purpose of preserving potassium and sodium, which have no action on it if water be not present. In many places the native naphtha is used to give light.

Reichenbach found that coal, distilled with water, yielded a little of an oil very similar to petroleum.

All the above substances are formed by the decay or destruction of organic matter, chiefly wood. It is not altogether improbable that those kinds which, like the Rangoon petroleum, contain paraffine ready formed, may have been formed by the action of heat on beds of vegetable remains, situated pretty deep in the crust of the earth.

Soot and *Lamp Black* are produced by the imperfect combustion of organic matters. They contain much carbon, mixed, in soot, with an acid resinous matter, and with a substance analogous to humus, but containing nitrogen, and called asboline. Lampblack, besides a little resin and oily matter, often contains naphthaline, which may be extracted by alcohol.

SULPHURISED AND NUTRITIOUS ANIMAL AND VEGETABLE PRINCIPLES.

We have already seen that some essential oils contain a large proportion of sulphur, and it is probable that these oils are derived from the decomposition of compounds existing in the plants which contain much sulphur, but the true nature of which is not yet known. But while such compounds only occur in a few plants, there is another class of sulphurised compounds which occur in all plants without exception. These compounds contain nitrogen and oxygen, both in considerable proportion to the carbon and hydrogen, and a small proportion of sulphur. They are all solid, and when heated yield products containing ammonia and sulphur. They have neither a medicinal nor a poisonous action on the animal system, but are nutritious in the strict sense of the word.

Such are vegetable albumen, vegetable fibrine, and vegetable caseine, as well as animal albumen, animal fibrine, and animal caseine. The latter, when compared with the former respectively, are found to differ from them only in form, agreeing with them in all essential chemical characters. Every one of the six dissolves in strong hydrochloric acid, gently warmed, with a purple colour; and all of them likewise dissolve in caustic potash, forming a solution which (after all the sulphur has been converted into sulphuret of potassium by boiling) gives, on the addition of acetic acid, sulphuretted hydrogen gas, and a gelatinous precipitate, which in every case is the same substance, called *Proteine,* by Mulder, its discoverer. Hence the above substances are called *proteine compounds,*—not that we can prove them to contain proteine ready formed, but because they all yield proteine in the same circumstances.

1. *Vegetable Albumen* has only been studied as yet in the coagulated or insoluble state. It occurs, however, dissolved, or in the soluble form, in vegetables, and especially in the oily seeds, along with caseine. It is always combined with alkali, to which it owes its solubility. Its distinguishing character is that of coagulating or becoming insoluble when heated to from 140° to 160°. Once coagulated it no longer dissolves, even in the liquid in which it was formerly quite dissolved. When a fresh vegetable juice is filtered and boiled, it yields a coagulum, which is nearly pure albumen. Its solutions are also coagulated by acids, by infusion of galls, by creosotes, and by corrosive sublimate. When dried, it is translucent. In all these characters it agrees with animal albumen.

2. *Vegetable Fibrine* is the essential part of what is called the

gluten of wheat. It is chiefly found in the seeds of the cerealia. When wheat, softened in water, is kneaded under water in linen bags to obtain the starch, and the residuary masses are beat up with rods, the pure fibrine adheres in elastic, transparent filaments to the rods. These, after being treated by ether, to remove fat oil, are pure fibrine. When dried, it becomes greyish and translucent, like horn. When heated, it yields the usual products of animal matters; and when left to itself in the moist state, it putrefies, disengaging fetid gases. It is quite insoluble in water. Diluted phosphoric and acetic acids dissolve it easily: these solutions are precipitated by ferrocyanide of potassium, and by infusion of galls. Diluted potash also dissolves it; and this solution, when neutralised by phosphoric or acetic acid, yields a precipitate which dissolves in an excess of either of these acids.

3. *Vegetable, Caseine.* Syn. *Legumine,* is an essential part of the seeds of the leguminosæ, and also of the oily seeds. It is only known in combination with acids and with alkalies. To obtain it, kidney-beans, lentils, or pease, are softened in water, then brayed in a mortar, the pulp mixed with much cold water, and strained through a fine sieve, which retains the husks, and allows the caseine and starch to pass, the former dissolved, the latter suspended. On standing, the starch settles to the bottom, leaving a solution of caseine, which may be decanted. It is sometimes milky if much oil be present, sometimes clear. When exposed to the air, it quickly becomes acid, lactic acid being formed, and coagulates exactly as skimmed milk does when it becomes sour. The solution of caseine does not coagulate by heat, but, like milk, forms a pellicle which is renewed as fast as it is removed. It is coagulated by the addition of an acid, and the coagulum dissolves in an excess of all vegetable acids, except acetic acid, which with mineral acids produces a permanent precipitate. This precipitate is well washed with cold water, alcohol, and ether, dissolved in hot water with a little ammonia, and this solution is precipitated by alcohol. It still contains ammonia, but is otherwise nearly pure.

In this state it is like paste of starch, and when dried it is nearly transparent, and liquefies when heated. In water it softens, and this paste is coagulated by acids, corrosive sublimate, infusion of galls, and creosote. Caseine is very soluble in tartaric and oxalic acids, also in caustic and carbonated alkalies if diluted. The coagula, or precipitates formed by mineral acids in solutions of caseine, are compounds of caseine with the acid: they are soluble in strong acids.

4. *Emulsine,* or *Synaptase,* is the name given to a peculiar compound of this class, found in certain oily seeds, as in almonds, &c. An emulsion of these seeds is very like milk. On stand-

ing, the oil rises, like cream, to the top, and the watery liquid is *now* coagulated by acetic acid, as milk would be. It coagulates also by boiling; and in this case, the whey, separated from the coagulum, again coagulates on standing 24 hours, and is found to contain lactic acid. The emulsine agrees with albumen, in being coagulated by heat, and with caseine in being coagulated by acetic acid. It exerts a peculiar decomposing agency on amygdaline, in which it is also itself decomposed.

Fungine is the substance of which mushrooms are chiefly composed. Its true nature is uncertain, but it contains nitrogen.

Gliadine is the name given to the viscid ingredient of gluten. It contains sulphur, and approaches in composition to vegetable albumen. It is probably a mixture.

When a vegetable juice, containing one or more of these compounds along with sugar, is exposed to the air, oxygen is absorbed, and a change is commenced in the albumen, fibrine, caseine, gluten, &c., which is soon communicated to the sugar, causing it to undergo the vinous fermentation. The temperature rises, and occasionally the viscous fermentation takes place, producing lactic acid, gum, and mannite. During fermentation, a grey deposit is formed; this is yeast or ferment. When the whole of the azotised principles have not been decomposed or rendered insoluble, the liquid, if excluded from air, remains without further change: but if air be admitted, the alcohol is converted into acetic acid, oxygen being absorbed by the azotised matters, the contact of which causes the alcohol also to absorb oxygen. When the sugar is in excess, only part of it is converted into alcohol, and part of the azotised matter takes the form of insoluble yeast, the rest being decomposed. The saccharine and spirituous liquid undergoes no further alteration. All the above statements apply to the juice of the grape and to the formation of wines and vinegar.

When the juice, as that of the grape, contains tartaric acid, ethers are formed, which give the liquid a peculiar smell and flavour, such as œnanthic ether, which is characteristic of all wines. When a juice contains sugar and caseine, it is most apt to undergo the viscous fermentation, or, at least, the caseine favours the production of lactic acid from the sugar. But at a high temperature, such as 100°, butyric acid is formed, instead of lactic acid.

Vegetable fibrine, as it is found in wheat flour, is subject to continual alteration by contact with water; and in this state it has the singular property of converting starch into dextrine, a soluble gum, and then into sugar. This remarkable power is best seen in germinating grain, as in malt, of which a small part mixed with a large quantity of starch in a thick paste, and warmed to 150° or 160°, very soon renders the whole quite fluid and dissolved, and finally converts it into grape sugar. That part of the fibrine which acts on the starch has become soluble in water. It is called *diastase.*

Diastase is made by rubbing up malt with a little water, expressing the mixture, adding just enough alcohol to separate the albumen, and to allow the liquid to filter. The filtered liquid, mixed with more alcohol, deposits the diastase. It is purified by being repeatedly dissolved in water and precipitated by alcohol. It is finally dried at a temperature of 100° or 110°. Thus prepared, diastase cannot be a pure compound, but it possesses in a high degree the power of promoting the solution of starch, that is, its conversion into dextrine and sugar. One part of diastase can convert into dextrine, with a little sugar, no less than 2000 parts of starch. Diastase is evidently fibrine altered, and still more prone to change. Its solution cannot be kept, it becomes acid, and loses its action on starch.

Malt is made by softening barley in water, and then exposing it to the air in moderately thick layers, at a moderate temperature, turning it frequently. In about four days the seeds germinate, if they have not been allowed to become too hot, and if the air has had free access. As soon as the germ has acquired the length of the seed, the operation is checked by drying the seeds in a current of warm air. They now constitute malt. In this operation, much carbonic acid is given off, oxygen being no doubt absorbed; the azotised matter in the seeds has undergone a change, and has acquired the properties of diastase; and the starch has in part disappeared, its place being supplied by grape sugar and dextrine.

When the malt is infused in warm water, the metamorphosis of the starch is completed, and the whole dextrine passes into sugar, which dissolves, along with extractive matter and salts. The solution is called *must.* When sufficiently concentrated, hops and yeast are added, and fermentation being carried on, the result is *beer* or *ale*, according to the strength of the must. When the malt has been in part roasted, the beer becomes very dark-coloured, as in the case of *porter.*

To obtain grain spirit, the meal, either of barley, oats, or rye, or a mixture, is digested in warm water along with 1 part of malt for 4 of meal, till the mass, at first thick, becomes fluid, a proof that all the starch has been metamorphosed. Yeast is then added, and, after fermentation, the must or *wort* as it is called, is distilled and rectified. Potato spirit is obtained in the same way, only using potato starch, instead of barley meal or rye flour.

Many other vegetable matters, and many fruits, may be made to yield spirit, malt or diastase being used in all cases where starch is to be converted into sugar.

Potato spirit is accompanied by the hydrated oxide of amyle, or oil of potato spirit: grain spirit by an oily matter, consisting chiefly of margaric and œnanthic acids, probably in part as margaric and œnanthic ether, and of a volatile oil, called by Mulder *oleum siticum*, that is, oil of grain. Wine spirit, that is, *brandy*, contains œnanthic ether, and the spirit of molasses, or *rum*, owes its flavour to butyric ether. The oils which contaminate potato and grain spirit are offensive and even injurious to health: they are included by the Germans under the general term *fuseloel*.

Panification. Bread may be made from any flour containing, as all good flour does, vegetable fibrine, sugar, and starch. The flour being made into a paste with warm water, and yeast being added, it is set aside in a warm place. After a time, more flour is kneaded into the mass, which has begun to rise, and the whole is now heated in the oven, or baked. The yeast induces the vinous fermentation in the sugar of the flour, and the alcohol and carbonic acid escaping, raise the bread and render it porous. The starch in general is little changed, but the sugar disappears, as well as a part of the gluten or fibrine. To avoid this loss, bread is now raised by means of carbonate of soda or ammonia and a diluted acid, which are added to the dough, and the effect is perfectly satisfactory. Equally good or better bread is obtained, and the quantity of flour which will yield 1500 loaves by fermentation, furnishes 1600 by the new method, the sugar and fibrine being saved. The addition of a little alum to the dough is useful in arresting that decomposition in the flour which is apt to occur if it have been kept in a moist place. Too much alum cannot be introduced, as it would prevent the fermentation.

The nutritive properties (using the word in its strict sense) of different kinds of flour or meal is directly proportional to the fibrine or albumen they contain; because it is these substances alone which can be converted into blood or flesh. Hence a working man requires more oat bread than wheat bread to restore the daily waste of the body, oatmeal containing much less fibrine &c. than wheat flour. The starch is consumed in the body, up to a certain point, but beyond this it is discharged in the excrements. We shall see hereafter what its function probably is. Even the best wheat flour contains more starch than is consumed; and the excess is greater in other grains.

In germination, the azotised principles of the seeds become soluble and prone to further change. When now dissolved, they are in the same state as those of the grape juice which at once cause fermentation when air is admitted. Diastase is merely gluten, that is, fibrine, in this soluble form or period of change.

When left in water, gluten swells, putrefies and disengages carbonic acid, hydrogen, and sulphuretted hydrogen gases: it then becomes fluid and ropy, the water becomes very acid, and contains a peculiar compound called caseous oxide, with acetate, phosphate and caseate of ammonia. When vegetable caseine putrefies, it gives out the odour of putrid cheese, and yields sulphuretted hydrogen gas.

Ferment, Yeast, Lees of Wine. These are names given to the deposit formed in fermenting liquids, which possess the property of exciting fermentation in must, wort, grape juice, infusion of malt, or solution of sugar. When solution of sugar is employed in excess, the ferment gradually diminishes, till about 15 per cent. are left, of a substance containing no nitrogen, and insoluble. This is *cellulose*, or *hordeine*. On the other hand, in grape juice, or infusion of malt, the ferment is reproduced from the azotised principles present.

Mulder and Schlossberger have shown that ferment is composed of regular cells, formed of cellulose, and containing an azotised matter, very easily decomposed, which is a proteine compound. This body rapidly decomposes the deutoxide and persulphuret of hydrogen, but loses this property after it has been heated to 212°. Mulder thinks that, after boiling, it is a superoxide of proteine.

The power of yeast or ferment to act on sugar is destroyed by boiling water, by absolute alcohol, by pyroligneous acid, salts of mercury, essential oils, sulphurous acid, &c.

Caseous Oxide, *Caseic Acid*, or *Aposepidine*, are names given to the crystalline compound formed during the putrefaction of gluten under water. It contains nitrogen, but its formula is unknown. It is soluble in water, insoluble in alcohol.

We now proceed to the consideration of the parallel compounds, *animal albumen*, *fibrine*, and *caseine*.

5. *Animal Albumen* is hardly known in a state of purity. The purest appears to be that prepared by exactly neutralising serum of blood or white of egg with acetic acid, and adding a large quantity of water. The albumen separates in translucent flocculent masses, which, when washed with water, assume the aspect

of paste. (Denis.) Albumen is best known in the form of the serum of the blood and that of white of egg.

Serum of blood, dried in a very gentle heat, leaves a translucent mass, which dissolves completely by digestion with water Both in this form, and in the preceding, it dissolves far more easily in the most diluted alkaline solutions.

White of egg consists of very delicate cells, filled with a ropy liquid. By beating with water, the cells are broken, and are afterwards deposited, being insoluble. Dried at a gentle heat white of egg is yellow, translucent, and brittle. In water it again softens into its original state. When calcined, it leaves 6 or 7 per cent. of salts, common salt, carbonate, phosphate, and sulphate of soda, and phosphate of lime.

The action of heat on albumen is remarkable. When heated alone, or after dilution with water, to between 145° and 165°, it coagulates into the well-known white elastic mass, which, when dried, becomes yellow, horny, and brittle. It is now quite insoluble in water; but if, after being coagulated and dried, it is placed in water, it swells up into the original elastic mass of coagulated albumen.

The albumen prepared by the process of Denis dissolves readily not only in acids and alkalies, but also in neutral salts, such as nitrate or sulphate of potash or soda. It is owing to the presence of such salts in serum and white of egg that their albumen is soluble in water. When the pure albumen of Denis is dissolved in solution of nitre, it is coagulated by boiling exactly like serum.

Solutions of albumen are coagulated by acids; the addition of free alkalies prevents even the action of heat. Serum and white of egg, when mixed with water, being both alkaline, may be neutralised carefully by acids, without coagulation. Acid solutions of albumen are precipitated by corrosive sublimate and ferrocyanide of potassium, by infusion of galls, by creosote, and by alcohol. The real difference between soluble and insoluble or coagulated albumen is not yet known.

When albumen putrefies, it yields sulphuret of ammonium, sulphuretted hydrogen, and other products. When heated, it burns with the odour of burnt horn or animal matter.

6. *Animal Fibrine* is found in blood, chyle, and lymph dissolved, and forms the chief part of the muscles. It may be obtained by whipping up blood with rods, when it adheres to the rods, and is finally purified by kneading with water to remove colouring matter, and by digestion with alcohol and ether, which dissolve fatty substances. When dry it is somewhat similar to albumen, and when heated burns with the same smell, leaving from 0·77 to 2·55 per cent. of ashes, phosphates of lime and magnesia.

Recent fibrine loses, in vacuo, about 80 per cent. of water, the greater part of which it again takes up when placed in water. When long boiled with water, it slowly dissolves; and when left long, that is, for some months, under water, it gradually disappears.

The fibrine of venous blood dissolves, at a gentle heat, in solutions of acetate of soda, sal-ammoniac, and nitre. These solutions are coagulated by heat, and exhibit the properties of dissolved albumen. Muscular fibrine may also be thus dissolved; but neither arterial fibrine, nor the fibrine of the buffy coat, can undergo this change. Venous fibrine loses this property by exposure to the air, when it absorbs oxygen and gives off carbonic acid. Fresh fibrine rapidly decomposes deutoxide of hydrogen: but boiling water or alcohol deprive it of this property.

The most striking character of fibrine is its spontaneous coagulation, as in the blood; which is also seen in vegetable fibrine in some juices. In regard to acids and alkalies, fibrine acts like albumen.

7. *Animal Caseine* is chiefly found in *milk*. It is not known in a state of purity, but only combined with bases or acids, for both of which it has a powerful attraction. Uncombined caseine is insoluble: in milk it is dissolved by virtue of the potash which renders that fluid alkaline. If carefully neutralised by an acid, milk is not coagulated, but it is then coagulated by boiling. The coagulum or curd formed by excess of acids is very soluble in oxalic and tartaric acids, sparingly so in the mineral acids. This coagulum contains, along with caseine, a good deal of the acid employed.

The coagulum caused in milk by alcohol yields, when burned, 10 per cent. of ashes, chiefly phosphate of lime. What is called soluble caseine is a compound containing much potash. With lime, baryta, &c., caseine forms insoluble compounds.

Milk, or any other solution of caseine, when evaporated in the air, forms a pellicle, which is renewed as fast as it is removed. This is insoluble, and yields ashes containing lime and phosphate of lime.

Milk may be analysed by drying it up in vacuo, dissolving the butter by a mixture of ether and alcohol, and the sugar of milk and salts by cold water. The caseine remains in this way undissolved, the salts having been first removed.

When exposed to the air, milk undergoes a peculiar change. The caseine enters into decomposition, and this decomposition passes to the sugar of milk, which yields a little lactic acid, and this causes the caseine not yet decomposed to coagulate. But the decomposition continues: the sugar of milk is at last entirely converted into lactic acid, mannite and gum; and if the acid be neutralised, and fresh sugar added, it will undergo the same change as long as any caseine remains. This is the method followed for obtaining lactic and lactates. The coagulum, separated from the whey when first formed, and pressed out, forms cheese. In making the better kinds of cheese, the milk, instead of being allowed to coagulate spontaneously, is coagulated by contact with water in which part of the lining membrane of a stomach has been infused. This infusion is called rennet, and it acts by virtue of containing albumen or gelatine in a state of decomposition, which is at once communicated to the sugar.

When milk, spontaneously coagulated, is exposed to a heat of from 75° to 85°, without any addition, the sugar of milk passes into grape sugar, and vinous fermentation ensues. The fermented milk, distilled, yields a spirit containing traces of butyric ether.

If sugar is made to ferment with caseine at about 100°, carbonic acid and hydrogen gases are disengaged, and butyric acid is formed in large quantity.

The chief mineral substances in milk are potash and phosphate of lime, which are found in its ashes. The ashes also contain sulphates, although milk does not. The sulphuric acid in the ashes is derived from the oxidation of the sulphur of the caseine.

The proportions of water, caseine, sugar of milk, butter, and salts, are very variable in milk. It generally contains about 86 per cent. of water, 4 to 7 of caseine, 3·5 to 5·5 of butter, and 3 to 5·5 of sugar of milk and salts. For the best method of analysing milk, proposed by Haidlen, I must refer to the "Annalen der Chemie und Pharmacie, xlv., 274." By this method Haidlen obtained as follows:—

	From Cow's Milk.	Human Milk.	Do.
Butter	3	3·4	1·3
Sugar of milk, and salts soluble in alcohol .	4·6	4·3	3·2
Caseine and insoluble salts	5·1	3·1	2·7
Water	87·3	89·2	92·8
	100·0	100·0	100·0

The colostrum, or milk given immediately after parturition, differs from normal milk in containing 15 to 25 per cent. of albumen, with less caseine, butter, and sugar of milk.

The milk of bitches, according to Simon, contains from 14·6 to 17·4 of caseine, 16·2 to 13·3 of butter, and no sugar.

Cheese is caseine in a state of incipient or progressive decomposition or putrefaction. In the finer kinds of cheese, there is a large proportion of butter, and to the volatile acids of the butter may be ascribed the flavour of cheese. Some kinds of cheese are full of what are called eyes, that is, hollows, caused by the formation of bubbles of gas; and in these hollows a liquid is sometimes found, containing free ammonia, a product of decomposition, which greatly heightens the flavour. When the blue mould appears in cheese, it is in a state of rapid decay or eremacausis, and much ammonia is given off. Little is yet known of the chemical differences in the making of different kinds of cheese. The richest are made almost entirely from cream, as Stilton and Parmesan. Others, as Gruyère, Gloucester, Cheshire, and Dutch cheese, are made with fresh uncreamed milk, or mixtures of this with cream; and more or less salt is used, as well as different methods of coagulating, in different places.

Animal Mucus is somewhat analogous to albumen, when dry. In water, it softens and swells, like tragacanth. It is precipitated by picric acid. It contains sulphur.

8. *Horny Matter.* This name may be given to the substance of which the epidermis, hair, wool, silk, feathers, nails, claws, hoofs, horn, shell, and probably also sponge, are composed. All these substances dissolve in potash-ley when heated with it, giving off ammonia, and forming a solution from which, by neutralisation with acetic acid, a white gelatinous matter is precipitated. (See *Proteine.*) They all contain sulphur. Sponge leaves 3½ per cent. of ashes, among which is found iodide of potassium. All the above substances, when heated or burned, give out the same peculiar and well-known smell, known as that of burnt feathers.

COMPOSITION OF THE PRECEDING SUBSTANCES.

According to the researches of Mulder, Liebig, Dumas, and many other chemists, vegetable albumen, fibrine, and caseine, have all the same, or very nearly the same, composition, as far as concerns the carbon, hydrogen, nitrogen, and oxygen, including under oxygen the sulphur and phosphorus, which occur in small proportion. Thus we have, in vegetable

	Albumen.	Caseine.	Fibrine.
Carbon	54·74	54·14	54·095
Hydrogen	7·77	7·16	7·308
Nitrogen	15·85	15·67	15·659
Oxygen and sulphur, &c. . .	21·64	22·03	22·938
	100·00	100·00	100·000

The above are analyses, taken at random from a number by different observers. Gluten, as being formed chiefly of fibrine and a modified albumen, has the same composition.

We find, further, that animal albumen, fibrine and caseine, agree in composition. Thus we find, in animal

	Albumen.	Caseine.	Fibrine.
Carbon	54·803	54·668	54·443
Hydrogen	7·021	7·302	6·997
Nitrogen	15·677	15·683	15·824
Oxygen and sulphur, &c.	22·499	22·347	22·726
	100·000	100·000	100·000

The composition of horny matter, of mucus, of the inner coat of arteries, &c., is analogous to the above, but not identical with it.

PROTEINE.

The remarkable similarity in composition of all the truly nutritive substances, whatever their origin, is not confined to the proportions of the elements in 100 parts, but appears also to belong to their intimate constitution. Thus, when their solution in potash, boiled until the whole sulphur is removed, is neutralised with acetic acid, there is formed from every one of the preceding, a gelatinous precipitate, which contains neither sulphur, phosphorus, nor salts, and which Mulder calls *Proteine*, as being, in his opinion, the first or leading compound, from which all the others are derived.

Proteine is very soluble in acetic and phosphoric acids of any degree of concentration ; it dissolves in hot and strong hydrochloric acid with a deep blue or purple colour, which changes to black on boiling. The composition of proteine is as follows :—

Carbon	54·848
Hydrogen	6·959
Nitrogen	15·847
Oxygen	22·346
	100·000

That is to say, exactly the same as the organic part of albumen, &c. It is evident, therefore, that we may consider albumen, fibrine, and caseine, both animal and vegetable, as formed of proteine, along with alkaline and earthy salts, different in each case, and also along with a little sulphur and phosphorus, or, as in caseine, sulphur without phosphorus. We are not entitled to say that these bodies are actually compounds of proteine with salts, sulphur, &c., for, in truth, proteine is rather a product of decomposition than a compound pre-existing. But there is an advantage to the memory in taking the above view ; and, besides, it is certain that albumen, &c., all agree so closely in constitution as to yield the same product of decomposition.

When boiled with potash, proteine gives rise to three new products ; *erythroprotide*, *leuçine*, and *protide*.

Mulder deduces from the analysis of proteine the formula $C_{40}H_{31}N_5O_{12}$: Liebig prefers that of $C_{48}H_{36}N_6O_{14}$, which agrees as well with the results of analysis, and throws more light on certain transformations which occur in the body. Both formulæ are to be considered as tentative only.

Mulder obtained by long boiling of fibrine with water, a substance which appeared to be a binoxide of proteine, $= C_{40}H_{31}N_5O_{14}$. The same substance was found by him in the buffy coat of blood in inflammatory diseases ; and was also obtained along with proteine by Van Laer among the products of the action of boiling diluted potash on hair.

When fibrine and albumen are long boiled with water they yield, according to Mulder, a *teroxide of proteine*, $C_{40}H_{31}N_5O_{15}$.

By the action of chlorine on solutions of the proteine compounds there is formed a substance in white flocculent particles, nearly insoluble. This is *chloroproteic acid;* and its formula is, $C_{40}H_{31}N_5O_{12} + CO_3$. (Mulder).

Leucine crystallises in brilliant white scales, very soluble in hot water and alcohol, also in ether. With nitric acid it forms *nitroleucic acid.* This acid crystallises in needles. The composition of these products is not fully ascertained.

According to Mulder, *erythroprotide* is, $C_{13}H_8NO_5$, and protide, $C_{13}H_9NO_4$.

ACTION OF ACIDS ON PROTEINE COMPOUNDS.

When moist fibrine is placed in water acidulated with $\frac{1}{2000}$ of hydrochloric acid, it swells up to a jelly which finally dissolves, all except a few flocculi, to which Bouchardat gives the name of *Epidermose.* Albumen and vegetable fibrine undergo a similar change. Bouchardat gives to the dissolved matter the name of *albuminose ;* but it is either proteine, or binoxide of proteine. (Mulder).

When the buffy coat of inflammatory blood is boiled with water, the filtered liquid on cooling forms a jelly. This, according to Mulder, is tritoxide of proteine, and not gelatine, as supposed by Bouchardat.

When compounds of proteine are dissolved with the aid of heat in strong hydrochloric acid, they yield a purple solution, which becomes black on exposure to the air. It then contains sal ammoniac and humate of ammonia. We have on the one hand,

$$\left.\begin{array}{ll} \text{Proteine .} & C_{48}N_6H_{36}O_{14} \\ \text{Water .} & H_6\,O_6 \\ \text{Oxygen .} & O_4 \\ \left.\begin{array}{l}\text{Hydro-}\\ \text{chloric}\\ \text{Acid .}\end{array}\right\} & H_5\quad Cl_5 \\ \hline & C_{48}N_6H_{47}O_{24}Cl_5 \end{array}\right\} \text{yielding, on the other} \left\{\begin{array}{ll} \text{Humic Acid} & C_{48}\,H_{24}O_{24} \\ \text{Ammonia .} & N\,H_3 \\ \left.\begin{array}{c}\text{Sal}\\ \text{Ammoniac}\\ \text{5 eq.}\end{array}\right\} & N_5H_{20}\quad Cl_5 \\ \hline & C_{48}N_6H_{47}O_{24}Cl_5 \end{array}\right.$$

This reaction enables us to see how proteine might be formed from the elements of sugar and of ammonia, water and oxygen being eliminated. For, abstracting from the hydrochloric acid, and bearing in mind that humine or humic acid, $C_{48}\,H_{24}\,O_{24}$, is merely sugar minus water, grape sugar (dry) being $C_{12}\,H_{12}\,O_{12}$, and 4 eq. of it being equal to $C_{48}\,H_{48}\,O_{48}$; let us then suppose 4 eq. of grape sugar to lose half the water they contain, leaving this variety of humic acid, and to take up 6 eq. of ammonia. Let us further pursue the process, which is opposite to that above explained, and subtract 4 eq. oxygen and 6 eq. water, and proteine will remain. The reader will observe that we can actually, with the aid of hydrochloric acid, cause proteine to take up oxygen and water, and to produce or be resolved into ammonia and humic acid, and that this humic acid only differs from sugar by the elements of water. So that we may expect hereafter to reverse the process and to cause sugar or humic acid, taking up ammonia and giving off water and oxygen, to give rise to proteine. At all events it is evident that proteine might thus be derived from sugar and ammonia, which meet in plants; and although in general we are unable artificially to produce the more complex substances, and can only decompose or resolve them into less complex forms, yet there are, even now, some cases in which more complex molecules may be artificially formed by the coalescence of more simple ones; and it is probably, in these very circumstances, that the vital force interferes and modifies the results. We may represent as follows the conceivable change, (the converse of that actually observed), by which we may conceive proteine to originate from sugar and ammonia.

$$\left.\begin{array}{ll} \text{Sugar .} & C_{48}\quad H_{48}\,O_{48} \\ \text{Ammonia .} & N_6\,H_{18} \\ \hline & C_{48}\,N_6\,H_{66}\,O_{48} \end{array}\right\} = \left\{\begin{array}{ll} \text{Proteine .} & C_{48}\,N_6\,H_{36}\,O_{14} \\ \text{Oxygen .} & O_4 \\ \text{Water . .} & H_{30}\,O_{30} \\ \hline & C_{48}\,N_6\,H_{66}\,O_{48} \end{array}\right.$$

The action of nitric acid on proteine compounds gives rise to xantho-proteic acid, an orange-yellow insoluble mass, not crystalline. Its formula is, $C_{34} H_{24} N_4 O_{12} + 2HO$. (Mulder).

Muscular fibrine, in contact with oil of vitriol, becomes gelatinous and dissolves. This solution, mixed with 2 vol. of water and boiled, yields sulphate of ammonia, leucine, and a syrupy substance sweet and soluble in alcohol. Gelatine, in the same circumstances, yields sugar of gelatine, and a fermentescible sugar, probably sugar of grapes.

GELATIGENOUS TISSUES.

Under this head we place several tissues which yield to boiling water a substance which on cooling forms a jelly, or may be called *gelatine*. They are chiefly found in the cellular membrane, the skin, the membranes in general, the tendons, ligaments, bones, cartilages, &c.

The cellular tissue and the membranes are chiefly formed of gelatinous matter, which is insoluble in cold water and acids. It combines with salts, as corrosive sublimate, persulphate of iron and alum, forming insoluble compounds which do not putrefy, as gelatine itself so readily does.

The gelatine of the skin, when moist, combines with tannic acid, if steeped in a solution of that acid, and is converted into leather. While the true skin is gelatinous, the epidermis is more allied to horn.

Chondrine is the name given to the gelatine of the cartilages.

Gelatine or *Glue* is that given to the gelatine of the bones and hoofs, skins, &c. of animals. Isinglass is made from the air-bladder of fishes, and is nearly pure gelatine.

1 part of pure gelatine, dissolved in 100 of hot water, forms a jelly on cooling. A solution of isinglass is completely precipitated by infusion of nut galls.

Chondrine and gelatine, in solution, are distinguished by acids, alum, and salts of lead, which precipitate chondrine but not gelatine. In regard to other tests, they agree. $\frac{1}{5000}$ of either may be detected by tannic acid.

By the action of chlorine on gelatine, there is formed what is called *chlorite of gelatine*, consisting, according to Mulder, of chlorous acid and gelatine.

By the action of potash, gelatine is converted into sugar of gelatine, or into a mixture of sugar of gelatine and leucine.

Sugar of gelatine crystallises in prisms, very soluble in water, and very sweet. With nitric acid it forms an acid, nitrosaccharic acid, which forms white transparent prisms, fusible and very soluble; it forms salts, which for the most part crystallise.

According to Mulder, sugar of gelatine is $C_8 H_9 N_2 O_7 = C_8 H_7 N_2 O_5 + 2HO$; and it forms with metallic oxides compounds of the formula $C_8 H_7 N_2 O_5 + 2MO$. Nitrosaccharic acid is $(C_8 H_7 N_2 O_5 + 2NO_5) + 4HO$; and its salts are $(C_8 H_7 N_2 O_5 + 2NO_5) + 2MO + 2HO$ or $(C_8 H_7 N_2 O_5 + 2NO_5) + 3MO + HO$. But, according to Boussingault, sugar of gelatine is $C_{16} H_{18} N_4 O_{14} = C_{16} H_{15} N_4 O_{11} + 3HO$. The proportions are the same as in Mulder's formula, but doubled, and the compound is supposed to contain 3 eq. of basic water. But in the compounds of the sugar with bases, these 3 eq. of water are replaced by 4 of oxide, giving the formula $C_{16} H_{15} N_4 O_{11} + 4MO$, which is the double of Mulder's formula, plus 1 eq. water.

The nitrosaccharic acid in crystals, according to Boussingault, is $C_{16} H_{18} N_4 O_{14} + 4NO_5 + 6HO = C_{16} H_{17} N_8 O_{33} + 7HO$. When dried at 230° it is $C_{16} H_{17} N_8 O_{33} + 4HO$, and its salts correspond, being as follows, $C_{16} H_{17} N_8 O_{33} + 4MO$. If we double Mulder's formula, for the sake of comparison, we obtain $C_{16} H_{14} N_8 O_{30} + 8HO$ for the acid, and for the salts $C_{16} H_{14} N_8 O_{30} + 4MO + 4HO$. It will be seen that in regard to the nitrosaccharic acid, Boussingault's formula differs from Mulder's in containing 1 eq. of water less, instead of more, as in the sugar of gelatine.

The nitrosaccharates crystallise very easily. That of copper, according to the very recent experiments of Verloren, is $C_{16} H_{14} N_8 O_{30} + 2HO + 6CuO$.

Gelatine does not yield proteine by the action of potash, and therefore does not belong to the series of the proteine compounds. Liebig adopts for gelatine the formula $C_{48} H_{41} N_{7\frac{1}{2}} O_{18}$; and for chondrine, $C_{48} H_{40} N_6 O_{20}$. The arterial membrane he supposes to be $C_{48} H_{38} N_6 O_{16}$. The latter is equal to proteine, plus 2 eq. water; and chondrine is equal to proteine, plus 4 eq. water and 2 eq. oxygen. It is easy, therefore, to see that gelatine is not fitted for nutrition of the body generally, since it cannot yield blood, which is only formed by proteine compounds. Gelatine may contribute, however, to the nutrition or supply of the gelatigenous tissues.

Bone. The gelatine and other animal matters in healthy bone constitute from 37·5 to 44 per cent.; the rest is earthy matter. In rickets and mollities ossium, the cartilaginous matter amounts to from 63 or 70 to 80 per cent., and the phosphate of lime is diminished in proportion, not exceeding, in some cases, 12 or 13 per cent.

The proportions of gelatine and earthy matter vary in different animal species.

The earthy ingredients of bone are, phosphate of lime, carbonate of lime, fluoride of calcium, phosphate of magnesia, with small quantities of common salt, soda, &c.

Bone or *Ivory Black*, obtained by calcining bones in retorts, contains all the earthy and saline matters, with a large proportion of charcoal intimately mixed with them. It probably contains nitrogen. Qu ? as paracyanogen or mellone ?

THE BILE.

This animal fluid, collected from the liver in the gall-bladder, is slightly alkaline, and has a viscid, oily consistence. It has, when fresh, a golden-yellow colour with a tinge of green, and becomes darker when exposed to the air. Its taste is bitter and persistent, with a sweetish after-taste. It is perfectly miscible with water, and its aqueous solution froths like solution of soap.

When dried in the vapour-bath, bile leaves a yellow mass, which dissolves in alcohol, leaving undissolved a little mucus. The alcoholic solution is deep green, but may be decolorised either by animal charcoal, or by the câutious addition of baryta, which forms an insoluble compound with the colouring matter. The decolorised alcoholic solution of bile still contains cholesterine, which is separated by adding twice its volume of ether, which separates the bile as a thick syrup, retaining the cholesterine dissolved. The bile, if now dried up in the vapour-bath, leaves a transparent solid mass like gum arabic, perfectly soluble in water and in alcohol.

The solution of bile is precipitated by neutral acetate of lead, but the liquid becomes acid. If the free acid be neutralised, acetate of lead produces a fresh precipitate, the liquid again becoming acid. Tribasic subacetate of lead precipitates at once the whole of the organic matter of the bile, but an excess of the precipitant is apt to redissolve a part of the precipitate, which is also soluble in alcohol. Mineral acids cause a resinoid precipitate in solution of bile.

Bile in solution may be recognised by the property of striking a purple colour with solution of sugar and sulphuric acid.

Purified bile, when calcined, leaves a white ash, composed chiefly of carbonate of soda, with traces of phosphate of soda and common salt. The ash amounts to 12 per cent., of which upwards of 11 consist of carbonate of soda.

It is, therefore, evident that bile is composed of soda united to an organic compound, having the characters of an acid, although a feeble one, and in some respects analogous to the fatty and resinous acids. This compound, which is the whole organic or combustible part of the bile, is called *choleic or bilic acid*, and bile is the *choleate of soda*.

Choleic acid is best prepared by making an alcoholic solution of 8 parts of pure bile, and dissolving, with the aid of heat, in this, 1 part of effloresced (monohydrated) oxalic acid. The oxalate of soda separates in crystals. The filtered liquid, diluted with a little water, is digested with carbonate of lead, till all oxalic acid is removed. Any lead that may be dissolved is separated by sulphuretted hydrogen, and the filtered solution evaporated in the water heat. Choleic acid may also be obtained by the action of dry hydrochloric acid gas on a solution of pure bile in absolute alcohol, and by several other processes, of which one may be noticed. Pure bile is precipitated by subacetate of lead, and the precipitate brought with water to the boiling point. Sulphuric acid is now added, drop by drop, until the precipitate has lost its peculiar consistence. The liquid is then filtered, and any dissolved lead separated by sulphuretted hydrogen.

To purify choleic acid it is dissolved in a very small quantity of alcohol, and precipitated by ether, which retains in solution fatty matters. The probable formula of choleic acid is $C_{44}H_{36}NO_{13} = C_{44}H_{35}NO_{12}, HO$.

When dried in the water-bath, or in vacuo, over sulphuric acid, choleic acid, if prepared from decolorised bile, is colourless or nearly so, and has the aspect of gum. It is resinous and friable when dry, but its powder attracts moisture strongly, and becomes agglomerated together. Its solution is distinctly acid to test-paper. The addition of mineral acids causes a separation of choleic acid in oily drops, which are soluble in pure water.

Pure choleic acid, when heated on platinum foil, burns with flame, leaving a voluminous coal which finally burns away without residue of ashes. When choleic acid leaves an alkaline ash, it is because it contains undecomposed bile, choleate of soda ; in fact, it may be called acid choleate of soda, a substance which has been described as a distinct ingredient of the bile by several chemists.

Numerous analyses of pure bile (deducting the ashes) and of choleic acid, both prepared in many different ways, by different chemists, as Demarçay, Theyer and Schlosser, Kemp, Enderlin and others, agree so well together that no doubt can be entertained in regard to this point, that the bilic or choleic acid of ox bile is a substance of uniform composition, and that the acid in bile has the same composition as that which is obtained in the separate state by the processes above given.

Further, if the choleate of lead, purified from phosphate, chloride, &c. of lead by solution in alcohol, be acted on by carbonate of soda, choleate of soda (artificial) is obtained; and this salt, when pure, is found to differ in no one respect from pure bile, or natural choleate of soda, and is, therefore, regenerated bile. Its composition is the same as that of bile.

Choleate of soda has already been described as purified bile.

Acid choleate of soda has been at different times known as *biliary matter*, and as *bilifellic acid with excess of biline.* (Berzelius). But the biline of this chemist, and also his sugar of bile, are nothing more nor less than either pure bile or choleic acid. Platner has lately obtained the acid choleate of soda crystallised, which is a strong additional argument in favour of the opinion that the bile is a uniform and definite compound of choleic acid, and that all the numerous compounds described by Berzelius and others as constituents of bile, are products of the decomposition of choleic acid. This is a consideration of the utmost importance, with reference to the production of bile in the animal body, to its functions, and in short to chemical physiology.

Choleate of lead (basic). This salt, precipitated by subacetate of lead, has the characters of a plaster, as choleate of soda has those of a soap.

PRODUCTS OF THE DECOMPOSITION OF BILE.

1. *Choloidic acid.* This acid is formed by the action of hydrochloric acid, when boiled with bile. It differs from choleic acid in containing no nitrogen. Its formula is $C_{60} H_{50} O_{11}$. Its production is attended with the formation of *taurine.* Choloidic acid is resinous or rather pitchy in aspect, softened by the heat of boiling water, insoluble in water and ether, soluble in alcohol. Probable formula $C_{60} H_{50} O_{11} = C_{60} H_{49} O_{10}, HO$.

2. *Taurine,* $C_4 N H_7 O_{10}$. This substance is found in the liquid which has deposited the choloidic acid. When pure, it forms large prisms, neutral, with a cooling taste, soluble in water. It contains the elements of binoxalate of ammonia and of water: $2 C_2 O_3 + N H_4 O + 3 N O$.

3. *Cholinic acid.* This is another non-azotised acid, formed when bile is acted on by fusion with caustic alkalies, which disengage the nitrogen as ammonia. It resembles the fatty acids, or rather the resinous acids. It forms large transparent tetrahedra, soluble in alcohol and ether, nearly insoluble in water.

4. *Dyslysine.* This is the name given by Berzelius to a compound formed during the action of hydrochloric acid on bile. It is very sparingly soluble in hot alcohol. (Hence its name, from δυς, difficult, and λυσις, solution). It has a resinous aspect, and the formula $C_{60} H_{46} O_7$, that is, choloidic acid *minus* 4 eq. water.

The *fellic acid* and *cholinic acid* of Berzelius are mixtures of some of the above, or of other products, with unaltered choleic acid. They do not exist ready-formed in bile, according to Theyer and Schlosser.

5. *Cholic acid* (Gmelin). This is an acid, containing nitrogen, formed when choleate of lead is acted on by acetic acid. It forms fine needles of a sweet and pungent taste, very soluble in alcohol and in hot water. Its formula is unknown.

6. *Cholanic acid* is a resinoid acid, found in putrid bile, and very similar to choloidic acid, if not identical with it.

7. *Fellanic acid* accompanies the preceding. It forms transparent prisms, and may possibly be cholinic acid. At all events, it is not established as a distinct compound; but is a product, probably a mixed one, of some of the changes of so complex a substance as choleic acid.

The colouring matter of the bile when dry is reddish-brown, but dissolves in potash with a yellow colour, becoming greenish-brown in the air. Its solution, mixed with excess of nitric acid, becomes first green, then blue, violet, red, and finally yellow. The same changes of colour are seen in serum, chyle, or urine charged with bile, as in jaundice.

COMPOSITION OF CHOLEIC ACID.

The formula of choleic acid cannot be considered as ascertained with certainty; but the most recent and very elaborate researches of Theyer and Schlosser have led these chemists to adopt the formula $C_{44}H_{36}NO_{13} = C_{44}H_{35}NO_{12} + HO$, for *choleic acid*, and for *choleate of soda*, (bile) $C_{44}H_{35}NO_{12} + NaO$.

When fused with potash, choleic acid loses 1 eq. ammonia and 2 eq. carbonic acid, $(= C_2NH_3O_4)$ and leaves $C_{42}H_{33}O_9$. This is hydrated cholinic acid, or rather $C_{42}H_{32}O_8 + HO$.

When boiled with hydrochloric acid—

$$
\begin{array}{lcllll}
\text{3 eq. of choleic acid, hydrated} \quad . \quad . \quad . & = & C_{132} & H_{108} & N_3 & O_{39} \\
\quad \text{take up 13 eq. water} \quad . \quad . \quad . \quad . & = & & H_{13} & & O_{13} \\
\hline
\quad \text{In all} \quad . \quad . \quad . \quad . \quad . \quad . & = & C_{132} & H_{121} & N_3 & O_{52} \\
\quad \text{and lose 3 eq. taurine, } 3(C_4H_7NO_{10}) \quad . & = & C_{12} & H_{21} & N_3 & O_{30} \\
\hline
\text{leaving 2 eq. choloidic acid, } 2(C_{60}H_{50}O_{11}) & = & C_{120} & H_{100} & & O_{22}
\end{array}
$$

It has already been mentioned that 1 eq. choloidic acid, *minus* 4 eq. water, is equal to $C_{60}H_{46}O_7$, which is the formula of dyslysine.

BILIARY CONCRETIONS.

The calculi or concretions found in the gall-bladder are generally composed of cholesterine, with more or less colouring matter. Sometimes the cholesterine is so pure that alcohol dissolves it entirely and becomes hardly coloured; at other times colouring matter alone is found. The former case occurs in the human subject: the latter generally in the ox.

Lithofellic acid is an acid found constituting the mass of certain concretions called *bezoar orientale,* and said to be found in the stomach of certain antelopes; but which are, no doubt, biliary concretions.

Lithofellic acid is fusible, gives off when heated a fragrant vapour, and has when cut or rubbed in the concretion the lustre of wax. It dissolves in hot alcohol, and forms brilliant six-sided prisms, insoluble in water. Formula, $C_{42} H_{38} O_8$ (Ettling and Will) $C_{40} H_{35} O_7, HO$ (Wöhler).

Nitric acid converts it into a new acid containing nitrogen. Formula, $C_{40} H_{28} NO_{11}$.

When distilled, lithofellic acid loses 2 eq. water, and yields pyrolithofellic acid, $C_{40} H_{34} O_6$.

BRAIN AND NERVOUS MATTER.

This substance consists of water to the extent of about 80 per cent.; of albuminous matter, 7 per cent.; and of several peculiar fats, among which are cholesterine, and another beautifully crystalline fat, resembling cholesterine but distinct from it.

Cerebric acid. This is a fatty acid, peculiar to the nervous matter. It is purified by means of ether, which removes an oily matter, and by crystallisation in hot alcohol. It forms white granular crystals, slightly soluble in water, especially when hot, although the greater part is not dissolved but swells up into a gelatinous paste. It melts when heated, and when burned leaves a very acid coal. It contains both nitrogen and phosphorus, which distinguishes it from the ordinary fat acids. Its salts are very insoluble in alcohol, as well as in water.

Oleophosphoric acid. This acid is dissolved, in combination with soda, by the ether used in purifying cerebric acid; but it is hardly known in a state of purity, being mixed with a neutral oil, *cerebroleine,* with cholesterine, and with cerebric acid, in small quantity. With alkalies it forms soaps, exactly similar to the salts dissolved from brain by ether. When boiled with water or alcohol, it is resolved into *cerebroleine* and phosphoric acid. Of the latter it yields about 2 per cent.

Cerebroleine is purified by cold alcohol, which dissolves the oil, leaving undissolved all cholesterine and cerebric acid. Its composition is the same as that of the oleine of human fat.

The cholesterine of the brain appears to be identical with that of bile. The brain also contains traces of oleic and margaric acids. When it putrefies, the oleophosphoric acid disappears entirely.

The most important point in the chemical history of the brain is that it contains both fat and albumen, the two extremes of the animal products, and substances (cerebric and oleophosphoric acids) of a composition intermediate between that of albumen and that of fat. These bodies, however, appear to contain even a larger proportion of phosphorus than albumen. It is not yet known where the cerebric and oleophosphoric acids are produced: whether in or by a special organ, as the bile is by the liver; or whether in the circulation generally. It will be seen hereafter that the blood does contain traces of cholesterine and other fatty matters; and, indeed, as the blood also contains bile, it may be supposed that the liver does not form the bile but merely separates it from the blood, it having been previously formed. In like manner, even if there should be found an organ connected with the formation or secretion of nervous matter, still the function of that organ might be only to separate cerebric acid, previously formed, from the blood. At all events, we cannot doubt that the very remarkable composition of the acids of the brain has an important relation to the functions of that organ, and that the production of those acids forms an essential part of the vital process going on in the body.

GASTRIC JUICE.

This juice, as extracted from the stomach of executed criminals, is colourless or slightly yellow, turbid, and distinctly acid. It contains free acetic and hydrochloric acids along with chlorides of potassium and sodium.

The property of dissolving or digesting food such as albumen, fibrine, caseine, &c., is owing in part to the presence of free hydrochloric acid, and in part to the presence of part of the lining membrane of the stomach dissolved, and in a state of change. The gastric juice converts into chyme, or digests, albumen, fibrine, &c., out of the body as well as in it, if the temperature of the stomach be kept up; and water acidulated with a trace of hydrochloric acid, and afterwards left for 24 hours in contact with the lining membrane of a stomach, acquires in a very high degree the solvent power of the gastric juice. Water thus prepared dissolves in 8 to 12 hours at the temperature of from 86° to 104° hard-boiled white of egg, &c., which requires 4 days at a temperature of 158° to 176° to be dissolved by water merely acidulated with the same proportion of acid, but not placed in contact with the stomach. This latter fluid, however, dissolves meat better than it does albumen, because the meat supplies some membranous matter in a state of change, by which the solution of the fibrine is finally promoted.

All attempts to isolate the supposed principle—*pepsine* as it was called, which is supposed by some to be the solvent of food in the stomach—have failed. The gastric juice has only yielded traces of animal matter, and we have not yet any proof that its solvent action depends on a peculiar compound, and is not rather the effect of a kind of fermentation induced in the food by contact with the particles of the dissolved epithelium, themselves in a state of change, and consequently of motion. Indeed, since this work was commenced, the existence even of free hydrochloric acid in the gastric juice has been denied, and it is very doubtful whether any free acid, such as lactic or formic acid, ever exist in the gastric juice in its normal state. On the whole, then, taking into account the facts of artificial digestion, it appears most probable that digestion is a process analogous to fermentation in the conditions under which it takes place, namely, a certain temperature, and contact with azotised matter in a state of decomposition; but differing from the usual forms of fermentation in its phenomena, no gas being disengaged, and its chief result being the solution of an originally insoluble matter.

SALIVA.

The chief use of the saliva is to assist in digestion, whether by itself containing animal matter in a state of change, or by its remarkable power of inclosing and retaining bubbles of air, the oxygen of which commences the change necessary to digestion, on coming in contact with the food or the stomach and gastric juice. To serve this purpose, the saliva has a very great degree of viscidity, so that it froths up easily, and the froth does not fall readily. It is alkaline, and contains hardly more than 1 or 2 per cent. of solid matter, partly mucus, partly the usual salts, partly a peculiar soluble matter, *ptyaline*. The salts of the saliva are the chlorides of potassium, sodium, and calcium, some potash, and soda, with a large proportion of bone earth. It appears also to contain a trace of sulphocyanide of potassium: at least it reddens with per salts of iron; and although acetates do this, there is reason to ascribe the effect here to sulphocyanides.

The *pancreatic juice* resembles saliva, but appears to be slightly acid, and contains 8 or 9 per cent. of solid matter, including ptyaline and a matter like caseine. This juice is added to the chyme in its passage through the duodenum, along with the bile and intestinal mucus.

EXCREMENTS. URINE.

The chyme, after receiving the pancreatic juice, the bile, and mucus, passes along the intestine, where the absorbents or lacteals take up the fluid part, leaving the insoluble portions. The chyle or absorbed fluid is partly conveyed into the abdominal veins, and partly made to pass through numerous glands (in which process it loses its acid reaction, becoming alkaline), from which it proceeds to the thoracic duct, and is then, with the lymph, poured into the vena cava to mix with the venous blood.

In the mean time, the insoluble parts of the chyme are rejected, and accumulate in the large intestines, various gases being disengaged, such as carbonic acid, hydrogen, carburetted hydrogen, nitrogen, and sulphuretted hydrogen.

The solid excrements of man contain very little matter soluble in water, and consist of woody fibre, with fatty, resinous, and waxy substances, and finally the insoluble salts of the food, namely, phosphate of lime and magnesia, with traces of soluble salts, and some silica.

The urine of man contains urea and uric acid, also hippuric acid, and other organic compounds very imperfectly known. It contains also phosphoric acid, magnesia, often ammonia, soda, phosphate of soda, common salt, sulphuric acid or sulphate of soda, in short, the soluble salts of the food, along with sulphuric acid formed by the oxidation of the sulphur of the tissues. The addition of ammonia to urine causes a precipitate of phosphate of lime.

Fresh urine, filtered (to separate mucus) into a perfectly clean vessel, keeps unchanged for weeks or even months; but if in contact with decomposing animal matter, the urea is speedily transformed, by putrefaction, into carbonate of ammonia, while phosphate of lime is precipitated, the urine becoming strongly alkaline.

The urine of the herbivora contains much uric acid, also hippuric acid: that of the carnivora contains more urea, and is strongly acid: uric acid predominates very greatly in the urine of birds, and that of reptiles is nearly pure urate of ammonia.

When benzoic acid is administered internally, it appears in the urine as hippuric acid, which latter acid is generally present in small quantity in urine. The acid reaction of human urine is not owing to lactic acid, as was formerly supposed, but to free uric acid dissolved by the phosphate of soda.

The salts of the urine and of the excrements, being derived directly from the food, vary according to its nature, the soluble inorganic salts of the food being found in the urine, the insoluble salts in the excrements. Thus, the ashes of the food of the carnivora contain no carbonates, but are rich in phosphates, and such also is the case with the salts (or ashes) of their excreta, liquid or solid. In fact, if we know the nature and composition of the ashes of the food, we can tell at once the salts of the urine. In an adult animal, the quantity of salts excreted is precisely equal to that contained in the ingesta, and therefore, by altering the food we can alter at pleasure the nature of the salts in the urine.

As an example, we may here adduce the case of the horse, which animal consumes, in his food, a certain quantity of mineral substances, derived ultimately from the soil :—

THE HORSE

Consumes of Mineral Substances,			Excretes of Mineral Substances,		
	oz.			oz.	
In 15 lbs. of hay,	18·61	21·49	In the urine . .	3·51	21·87
In 4·54 lbs. of oats,	2·46		In the fæces . .	18·36	
In water . .	0·42				

The above result is one obtained by actual and very careful experiment, and the nature of the salts is found to be the same, as indeed must obviously be the case, as long as the animal does not change its weight. A growing animal will retain the phosphates in part to aid in forming bone, and an old or wasting animal will give out more salts than are taken in.

It is obvious that analyses of urine or excrement are unnecessary if we can examine the food; and that in general they must be useless, since we can never expect the same result twice, unless where the food is not varied.

Guano, so highly prized as a manure, is the decayed excrement of sea fowls, which was originally, like that of reptiles, and indeed also of birds in general, mixed urine and fæces, the urine being solid or semisolid, and consisting of urate of ammonia. It varies much in the proportions of its ingredients, both because the original excrement must have varied according to the food of the birds in different places, and also because some specimens have not been so long exposed to air and moisture as others, and some are almost fresh. Thus some guano contains upwards of 30 per cent. of uric acid, while in other specimens hardly a trace of that acid is left. The better qualities of guano contain much ammonia, partly free or as carbonate, as proved by its odour, partly combined, as sal ammoniac, oxalate, urate, and phosphate of ammonia, and phosphate of ammonia and magnesia. They also contain phosphate of soda and phosphate of lime, the latter being derived from the bones of the fish on which the birds fed. There are also found sulphate of potash and soda, and oxalate of lime, in guano. The remainder is water, and a brown matter like humus.

It is easy to see that guano must act chiefly as a source of ammonia and of earthy and alkaline phosphates, so valuable to growing plants, especially to those cultivated for food ; and that its value depends very much on the amount of phosphates it contains. But while the value of guano is unquestionable, let us not overlook the fact, that while we are ransacking the most remote islands for guano, that substance supplies us with nothing but the mineral salts and the ammonia which have formed crops of vegetables and races of animals at some former period, and that it differs in no essential point from the fresh or modern excreta of man and animals nearer home, which excreta, at least those of man, the most valuable of all, we allow to be carried into the sea in quantities which may be measured by the food we consume. In fact we take out of the sea, in the shape of guano, only part of what we throw into it in the contents of our common sewers. These valuable matters, instead of being carefully collected and preserved, as in China, are sent to form the food of sea plants : on these plants animals feed, which animals serve as food to fish. The fish are consumed by sea fowl, and we recover in their excrement a part of what we are constantly throwing away. Another part of what we lose we recover in this country, at a great expense, in the shape of bone-earth, which, however, must be taken from other countries. We shall return to this subject : meanwhile, let us express a hope that Europe will at length follow generally, as in some districts it has done, the rational example set by the eminently practical Chinese, of restoring to the soil, as nearly as possible, in the shape of excreta, what we take from it in our crops and cattle, and thus keeping up its fertility.

URINARY CALCULI.

These are of various kinds, according to the peculiar condition of the urine.

Uric acid calculus is the most frequent, being the usual deposit when the urine is acid. Its origin, as a calculus or deposit, that is, in abnormal quantity, is owing to deficient aeration, much oxygen being required to resolve it into soluble compounds, such as urea, carbonate of ammonia, or even oxalic acid. Hence sedentary habits, highly carbonised food, and indulgence in strong wine, all favour its production: the first by diminishing the supply of oxygen, the two latter causes by seizing on the oxygen to the exclusion of the uric acid. It is easily recognised by the action of potash, which dissolves it, and forms a solution from which acids precipitate uric acid: or by nitric acid, which dissolves it with effervescence, and yields on evaporation of the solution a deep red stain, becoming purple with potash. Uric acid calculus is commonly tinged more or less red or brown. When pure it is entirely dissipated before the blowpipe.

Urate of ammonia also occurs, and is distinguished from uric acid by disengaging ammonia when dissolved in potash.

Phosphate of lime is very frequent when the urine is neutral or alkaline. It is white and earthy, soluble in nitric acid, and precipitated by ammonia. It is fixed in the fire.

Phosphate of ammonia and magnesia is also pretty frequent. It dissolves easily in acetic acid, and when heated gives off ammonia, leaving a solid mass soluble in acids.

Fusible calculus is a mixture of the two preceding. It melts readily before the blowpipe.

Oxalate of lime constitutes the mulberry calculus, and often appears as minute crystals in the urine. When heated, it leaves carbonate of lime; or if heated in a tube with oil of vitriol, it gives off carbonic oxide. It dissolves in acids, and is precipitated by alkalies.

Carbonate of lime occasionally, but very rarely, constitutes a urinary calculus, which is easily recognised by the action of hydrochloric acid, which dissolves it with effervescence, and by a red heat, which leaves quicklime.

Cystic oxide or *cystine*, and *xanthic oxide*, are very rare calculi. Their characters and composition have been given under *Uric Acid.*

LYMPH.

This fluid may be looked on as blood devoid of its colouring matter. When drawn from the vessels, it coagulates like blood, from the separation of fibrine; and the liquid in which the coagulum has formed itself, coagulates, when heated, like the serum of the blood. Human lymph contains about 96 per cent. of water, and variable proportions of albumen, fibrine, and salts, the salts amounting to nearly 2 per cent.

BLOOD.

This important fluid, from which the whole animal body is formed, and by which it is supplied and nourished, is a thick, somewhat viscid, liquid, of a slight saline taste, and a peculiar faint odour. It is deep red and opaque, and has a density of 1·0527 to 1·057.

It is made up of an immense number of *globules* or flattened disks, floating in a limpid yellowish fluid. When drawn, it soon coagulates, forming a trembling jelly, which gradually contracts, expressing a yellowish liquid, *the serum*, which is occasionally turbid, and is always alkaline to test paper, and saline to the taste.

The coagulation consists in the separation of the fibrine previously dissolved, which, owing to some unknown cause, assumes the insoluble state, forming a fine network or jelly, in which the globules are inclosed. If the blood be beat with a rod, the fibrine separates perfectly and adheres to the rod; but it is in the form of white filaments, and the globules remain suspended in the serum, no jelly whatever being formed in this case. Or if the fresh blood be mixed with 8 times its bulk of solution of sulphate of soda, no coagulum is formed, the fibrine remains dissolved, and a sediment is deposited which contains the globules unaltered.

The *red globules* thus prepared may be collected in a filter. Pure water added to them, or to the coagulum of blood, rapidly alters their form, and in fact dissolves them into an opaque liquid. This action of water is thus explained: the globules are formed of a thin, colourless, and transparent coat, inclosing a very soluble colouring matter. They float in a saline liquid, in which there is equilibrium between the contents of the globules and the fluid surrounding them. But when the latter is diluted with water, the equilibrium is disturbed, and endosmosis takes place, by which the contents of the globules acquire so greatly increased a volume, that the globules burst and their contents are dissolved in the water. The torn membranes of the globules may be detected by the microscope.

In saline solutions, the globules do not absorb water any more than in the serum. When collected in a filter, the globules form a red mass of the consistence of honey, consisting of fibrine and albumen, the latter in combination with the colouring matter. In a concentrated solution of chloride of calcium, the globules lose water by exosmosis, and contract in volume. If now placed in pure water, the globules again swell, and burst, forming a jelly which dissolves in water. The solution, on standing, deposits fibrine in white membranous masses, and the supernatant liquid, when boiled, is coagulated, indicating the presence of albumen.

The *colouring matter* of the blood is contained in the globules in combination with albumen, but is unknown in a state of purity. The compound of albumen and colouring matter is of a deep-red colour, becoming bright in contact with air or oxygen, and being rendered nearly black by carbonic and sulphurous acids, sulphuretted hydrogen and sulphurets. Protoxide of nitrogen gives it a purple colour.

The red compound gives 2 per cent. of ashes, of which $\frac{1}{3}$ is peroxide of iron; and iron is uniformly present in red blood, which is the only animal product in which it occurs. This iron cannot be detected in the globules or their contents by the usual tests, but after passing chlorine through the red solution till the colour is destroyed, the iron may be detected by ferrocyanide of potassium.

When the red compound of albumen and colouring matter above mentioned is moistened with oil of vitriol, so gradually as not to become warm, a pasty mass is obtained, which attracts moisture from the air and forms a red jelly. If this be very gradually rubbed up with pure water, it contracts into a dark-red matter, which is surrounded with a colourless or yellowish liquid. This liquid is found to contain all the iron, and the dark matter, when calcined, leaves a white ash, entirely free from iron, if the operation has been well performed. I have repeated this interesting experiment, first devised, I believe, by Sanson, which proves that, although the red compound contains iron, yet the colour does not necessarily depend on that metal; for the colour is altogether uninjured by the complete removal of the iron just described, although the colouring matter actually obtained in this experiment is not the original colouring matter of the blood, but modified.

The *Hematosine* of Lecanu is also a product of decomposition. It is prepared by means of diluted sulphuric acid, alcohol, and ammonia, by a tedious process. It is dark-brown, and forms red solutions with the alkalies, being insoluble in water, alcohol, and ether. It contains part of the iron of the blood, but as some kinds of homatosine contain $\frac{1}{4}$ or $\frac{1}{3}$ more iron than others, while its properties continue the same, it is obvious that the iron does not contribute essentially to those properties, such as the colour. Hematosine contains 6 to 8 per cent. of iron.

But the iron serves an important purpose in the blood; and we have reason to think that it is present in the form of oxide, for sulphuretted hydrogen and soluble sulphurets cause the blood to become first green and then black, owing to the formation of sulphuret of iron—a character indicating either the oxide or some corresponding compound, and not a compound like ferrocyanogen, in which the sulphurets cannot detect the iron

Moreover, we see that oil of vitriol dissolves out oxide of iron; and although alkalies and ferrocyanide of potassium do not detect it, this is owing to the blood being an alkaline liquid, and to the presence of so much animal matter.

It is from the blood that are formed the tissues, the cells, muscular fibre, nervous matter, &c. &c.; and we may, therefore, expect to find some relation between their composition and that of the blood. In fact, flesh, or muscular fibre, as it exists in the body, including vessels, nerves, fat, &c., has exactly the same composition as the blood has on an average of venous and arterial, or a mixture of both. We may, therefore, look on muscular fibre, or animal flesh, as simply blood more highly organised.

In addition to the substances mentioned above, namely, albumen, fibrine, colouring matter, and salts, blood also contains fat, apparently cholesterine, along with fatty acids and a peculiar fat, called *seroline.*

The normal proportions of serum and clot are 87 per cent. of serum to 13 of clot.

1000 parts of human blood contain 869·15 of serum, of which 790·37 are water, 67.8 albumen, and 10·98 of salts and fatty matter: along with 130·85 of clot, containing 125·63 albumen and fibrine of the globules, and 2·27 hematosine (along with a little fatty matter and traces of salts in all three), also 2·95 of fibrine, separate from the globules.

Venous blood contains more water and fewer globules than arterial blood.

The blood contains gases, chiefly carbonic acid and nitrogen, which it gives off in vacuo, or in a current of hydrogen. It is said to contain free oxygen, but this seems very improbable, when we reflect that fibrine absorbs oxygen, transforming it into carbonic acid, and that blood is instantly altered by contact with oxygen. The change from venous to arterial blood, from dark to florid, depends on the presence of oxygen, but also requires the presence of a saline solution. Indeed, a similar change of colour takes place in vacuo if the clot of venous blood be there covered with a pretty strong solution of various salts.

THE NUTRITION OF PLANTS AND ANIMALS.

The animal and vegetable kingdoms of nature are connected together in a beautiful system of mutual dependence, exhibiting a perpetual circulation of certain elements through both, the mineral kingdom being the point of departure and that also where the circulation terminates, to recommence unceasingly.

Plants derive their nourishment exclusively from the mineral world. It is clear that the first plants must have done so, and although the decaying remains of former plants now contribute to vegetation, we shall see that they do so under mineral forms, and not essentially: they promote vegetation, but are not indispensable to it.

The mineral food of plants, then, consists of carbonic acid, water, and ammonia, all of which are obtained from the atmosphere, and of sulphur (sulphuric acid), phosphorus (phosphoric acid), alkalies, earths, salts, and metals, all derived from the soil. Without the aid of the matters derived from the soil, the most abundant supply of carbonic acid, water, and ammonia, is of no use. But if a soil contain these necessary substances, plants will thrive in it, even if they have no carbonic acid or ammonia furnished in the shape of manure beyond the usual atmospheric supply.

During germination, oxygen is absorbed and carbonic acid produced: starch is transformed, probably by the action of diastase, or of an acid developed during germination, into sugar or dextrine, which being soluble, are fitted for being conveyed to all parts of the plant. Meanwhile the azoto-sulphurised ingredients of the seed also become soluble, and with the sugar, &c. contribute to the formation of new parts, destined to collect food from the air or the soil.

The leaves and roots, as soon as formed, absorb carbonic acid from the air and from the soil. Alkalies are at the same time taken up by the roots, and with their aid the carbonic acid, under the influence of light, is decomposed, its carbon being retained, while its oxygen is given off. At the same time, water, ammonia, sulphuric acid (or a sulphate), and phosphoric acid or phosphates are taken up, and their elements, along with the carbon, give rise to fibrine, albumen, caseine, &c.

It is probable that the fixation of carbon is a gradual process, having successive stages; that the carbonic acid is first reduced or deoxidised so far as to yield oxalic acid; thus $C_2 O_4 - O = C_2 O_3$; that oxalic acid, with the aid of water, is farther reduced, so as to yield malic or citric or tartaric acid: thus, $C_4 O_6 + 2 HO = C_4 H_2 O_8$; and $C_4 H_2 O_8 - O_4 = C_4 H_2 O_4$; this last formula doubled is that of anhydrous malic acid, $C_8 H_4 O_8$. From this and similar compounds, sugar, $C_{12} H_{12} O_{12}$, starch, $C_{12} H_{10} O_{10}$, gum, $C_{12} H_{10} O_{10}$, and woody fibre, $C_{12} H_9 O_9$ or $C_{36} H_{22} O_{22}$ are easily deduced, by the addition of the elements of water and the elimination of oxygen. Thus, 3 eq. hydrated malic acid, $C_{24} H_{18} O_{30}$, plus $6 HO$ and minus O_{12}, is equal to 2 eq. dry sugar of grapes $C_{24} H_{24} O_{24}$. There is good reason to think that the chief function of the alkalies in plants is to promote these metamorphoses.

Water not only acts by its elements, but also as the indispensable solvent through which the whole food of plants, especially that derived from the soil, can alone enter them.

From the above considerations we may draw several useful inferences.

1. The presence of decaying vegetable matter in the soil promotes vegetation by furnishing a steady supply of carbonic acid gas. The proportion of decaying matter or humus must not exceed a certain limit; otherwise there is too much carbonic acid in the air of the soil, and the plant dies in such circumstances.

2. The presence of decaying azoto-sulphurised matter in the soil is very advantageous, furnishing a supply of ammonia, which is essential to vegetation, and is scantily supplied by the atmosphere.

3. The supply of carbonic acid and of ammonia can only favour the development of vegetation in so far as alkalies and phosphates are supplied by the soil.

4. Since all the azoto-sulphurised principles, albumen, fibrine, caseine, &c., contain sulphur and phosphorus, or rather phosphates, it is evident that seeds and such other parts of plants as contain these principles can only be developed in so far as the soil contains alkaline or earthy phosphates and sulphuric acid or sulphates.

5. If the soil is rich in alkalies, sulphates, and phosphates, and if it also contain soluble silicates, essential to the stem of the grasses and cerealia, it is fertile for all nutritious crops; and such crops will, in that case, derive from the atmosphere alone all the carbon and nitrogen (carbonic acid and ammonia) they require, *provided time be allowed.* The advantage of decaying organic matter, or of manures containing ammonia, in such a soil, consists in shortening the time necessary for the development of the plant; a matter of the last importance in our uncertain climate, but of far less consequence in southern regions, where summer is perhaps twice as long.

6. The ashes of wood, straw, leaves, &c., consisting entirely of matter extracted from the soil by the plants for the purposes of vegetation, must prove a most fertilising manure: and in all cases the ashes of any crop must be the best manure for that vegetable.

7. But as the ashes of plants are represented by the excreta of the animals (or the ashes of these excreta) which fed on them, so the excreta of animals fed on turnips, hay, straw, potatoes, &c., must be the best manure for turnips, hay, corn, and potatoes, respectively.

8. When by the addition, to an average soil, of guano, or of bone earth, a very heavy crop is obtained, say of wheat, we are

not to expect that a repetition of the same treatment will produce the same effect. We must bear in mind, that the presence of the increased supply of phosphates has enabled the plant to take up a much larger quantity than otherwise it could have done, of alkalies, silicates, and the other necessary minerals. Since we have not added those substances in our guano or bone earth, it may happen that the soil is exhausted of its whole actually available supply of them by that one crop, and that years may elapse before it becomes, in the course of nature, as fertile as before.

9. The only certain rule is this: as far as possible to restore to the soil, in the shape of manure, exactly what it has lost in the crop ; if the soil were originally fertile this will maintain its fertility, which will even be gradually augmented by the action of the weather on the subsoil.

10. With a view to this, every particle of solid or liquid manure, especially human, should be preserved with the utmost care. It is their mineral elements which are the most valuable ; and since these have all come from the soil, in preserving them for manure we are only restoring what we have taken away. This has long been systematically done in China, and is also generally practised in the Netherlands ; but in this country the waste of valuable manure is lamentable, and is necessarily followed by a slow but certain deterioration of our soil and crops, which we are now endeavouring to remedy by the expensive, precarious, and partial measure of importing bone earth and guano. But guano will, ere long, be exhausted; and when other countries know the real value of their bone earth, they will not willingly part with it, at all events not except at a very high price.

11. If a soil is not fertile generally, it must be deficient in most of the substances above alluded to ; but if it yields good crops of one vegetable and not of others, it must be wanting in the characteristic mineral elements of the latter, which must then be supplied.

12. The ashes of plants being known, the fact that a certain vegetable, cultivated or wild, thrives in any given spot, furnishes us with an analysis of the available or soluble elements of the soil, and enables us to direct our measures of improvement according to the crop we wish to raise.

Although certain bases characterise the ashes of certain plants, as potash does those of turnips and potatoes, and lime those of peas, beans, &c. ; yet in many cases, one base may be substituted for another, as soda for potash, or magnesia for lime.

It is maintained by some that carbon is introduced into plants, in part, as humus, humic acid, or humate of ammonia, dissolved in the juice, and derived from the mould in the soil. But there is no evidence that fertile soils contain humus in a form soluble in water, and the sap, when first entering the plant, is colourless, while all solutions of humus, &c., are brown. Besides, in forest land, which is not manured, the proportion of humus or of carbon in the soil, instead of diminishing, rather increases, while enormous quantities of carbon are removed annually in the shape of wood. Here, as in the case of the first vegetables, it is plain that all the increase of carbon must be derived from carbonic acid: since, if the plant does absorb humus or humic acid, or humate of ammonia, which is not proved, it must give to the soil as much or more humus, &c., as an excretion from its roots.

It has also been argued by some that plants may obtain their nitrogen, either directly by absorption of the nitrogen of the atmosphere, or by causing that gas to form ammonia, combining with hydrogen derived probably from water, &c.; or, lastly, from the decomposition of nitric acid, which acid is supposed to be formed in the atmosphere by direct combination of its elements. But no evidence has ever been given, either that plants can absorb nitrogen directly, or that they can cause the nitrogen of the atmosphere to combine with hydrogen. As for nitric acid, although traces of it have been observed in thunder-storms, it does not appear to be formed in sufficiently large quantity;* and if it were, no proof has yet been offered that plants can derive their nitrogen from it. The action of nitrate of potash, or of soda, as manure, proves nothing, because it may be due to the alkalies alone, and probably is so, since they do not seem to act better than other salts of the same bases. Moreover, many plants, such as tobacco, and sunflower, contain much nitrate in their juices, and therefore appear rather to form nitric acid than to destroy it. On the whole, it appears nearly certain that ammonia is the only source of nitrogen in plants. It is self-evident that the atmosphere must contain ammonia, derived from the putrefaction of animal and vegetable matter, and also that, however small the *proportion*, the absolute quantity in the air at any one time must be sufficient for the supply of the vegetable world, and through it of the animal world, since all animals and vegetables ultimately putrefy, giving off their nitrogen in the form of ammonia. It is quite easy to detect ammonia in rain-water, by which means it is conveyed to the roots or leaves of plants; and it has also been proved that the juices of plants contain abundance of ammonia.

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* In fact, the proportion of nitric acid thus formed, is so very small as to lead to the conclusion that it is formed only from the ammonia present in the atmosphere. Should this prove true, as is highly probable, then ammonia will be the source of all the nitrogen of plants, even if part of that nitrogen should be derived from nitric acid. It is generally admitted that in nitrification the whole of the nitric acid is derived from the oxidation of ammonia.

The nutritious principles, albumen, fibrine, and caseine, are formed by plants alone from ammonia, sugar (or gum, starch, &c.), sulphates, and phosphates. They pass into the body of animals, and are there converted into blood. As they cannot be formed nor exist without the phosphates, so by their means the animal body is supplied with bone earth, and with the soluble phosphates necessary for the other tissues.

In the animal body, the leading and characteristic action is the absorption of oxygen and the oxidation of the tissues: that is, of carbon and hydrogen, so that animals take up oxygen, and give out carbonic acid. This is the reverse of what occurs in plants, which absorb carbonic acid, and give out oxygen.

In the lungs, oxygen enters the blood, and is carried, apparently, by the agency of a compound of iron, to every part of the body. The oxidation of the effete, or worn-out tissues, which have meanwhile been replaced by the blood, takes place in the capillaries, and is, in all probability, the source of the animal heat. The final result of this oxidation is the production of a large quantity of carbonic acid and water, which are given off by the lungs and skin.

Health, in the animal body, consists in the due balance or equilibrium between the oxidising, or destructive agency of the atmosphere, and the process of nutrition by which the other is compensated.

Since the nutritious, or blood-forming elements of food, have the same composition as the albumen, fibrine, &c. of the tissues—indeed, in the case of animal food, are identical with them—we may consider the process of oxidation and destruction, either as affecting the food directly, or, what is more probable, those portions of the tissues which, having performed their functions, are to be thrown off. But we must not forget that in the herbivora, a great part of the combustion which yields the animal heat is carried on at the expense of those parts of the food which cannot form blood: namely, sugar, starch or gum, fat, &c.

The fat of the animal body is, at all events in great part, derived from the non-azotised elements of the food when these are in excess, and oxygen is deficient. In these circumstances, the deficiency of oxygen is supplied at the expense of sugar, starch, or gum, which, by losing oxygen, gives rise to fat; for the proportions of carbon and hydrogen in sugar, &c., and in fat, are exactly the same, that of oxygen alone being different. Hence the conditions favourable to the formation of fat are, abundant farinaceous food, and rest, that is, defective aeration, as is seen in stall-fed animals, and in the fattening of geese fed on maize and deprived of the power of locomotion. The formation of wax, a species of fat, from sugar by the bee, is another example.

It is very interesting to remark that the composition of the chief elements of the bile, and the urine, bears a close and simple relation to that of the blood or tissues. If the formula of urate of ammonia be added to half that of choleic acid, the sum represents the composition of blood or flesh, or differs from it only by a very little water and oxygen, substances which take part in almost every chemical change in the body, water being always present in the body, and oxygen being introduced through the lungs. Now, urate of ammonia is the urine of birds and reptiles, and represents that of the mammalia; for uric acid, when further oxidised, yields urea and carbonic acid, while urea with the elements of water, passes, as in putrefying urine, into carbonate of ammonia. As for the bile, the other product of the destruction of the tissues (at least this is its origin in the carnivora, and partly in the herbivora), it undergoes resorption in the intestines, and is finally oxidised into carbonic acid and water, thus contributing to keep up the animal heat. The final result is, that the tissues, which may be supposed, with the addition of a little oxygen, to be resolved into choleic acid (bile) and urate of ammonia (urine), are entirely converted, or oxidised into carbonic acid, water, and ammonia.

The food of animals may thus be said to be literally burned in their bodies, and this, as in the case of other combustibles, for the purpose of producing heat. The gaseous products of the combustion are sent off through the skin and lungs, while the smoke, soot, and ashes are represented by the excrements and urine.

The food required by animals must bear a certain relation to the waste of matter, and to the heat required. Thus, a hard-working man, in whom the change of matter is rapid, requires much more food (blood, or proteine compounds) than a sedentary person; and in cold climates a much larger quantity of food rich in carbon, especially fat, blubber, and similar matters, is necessary than in warm climates, where, indeed, such food excites invincible repugnance. Any misproportion in the amount or nature of the food has a tendency to induce disease. Thus, Europeans, who often eat and drink as at home when they go to tropical countries, pay the penalty of their ignorance in the very frequent liver complaints observed among them. For the same reason, hepatic disease is more frequent during summer than during winter.

After death, the animal body is slowly, but surely, resolved into the ultimate products of putrefaction, namely, carbonic acid, water, and ammonia, which rise into the atmosphere, having completed the circuit through which we have traced them, in order to recommence it by once more contributing to the growth of plants on which animals will again feed.

The bones of dead animals are also by degrees restored to the soil from which they were taken ; and nothing is finally lost. Even the rich manure which we recklessly cast into the sea, serves as manure for sea plants, on which are fed fish, which, in their turn, become food for sea fowl, the excrements of these last, in the shape of guano, returning to fertilise the fields from which their mineral elements were perhaps originally taken.

It is evident that there must be a balance or equilibrium kept up between the animal and vegetable worlds. For the atmosphere in which both live does not, at least perceptibly, change in its composition. There is no appearance either of increase or diminution, in the proportion of oxygen, or in that of carbonic acid. Yet we know that animal life tends directly and powerfully to increase the proportion of carbonic acid, and to diminish that of oxygen, while the tendency of vegetable life is exactly the reverse. Hence if, in any quarter, population or animal life extends, a corresponding augmentation of vegetable life must somewhere be the result ; or if, by cultivation, the amount of vegetation in any quarter is increased, the inevitable consequence must be an extension of animal life, otherwise the air would become richer in oxygen. As both carbonic acid and ammonia are partly supplied to the atmosphere from the earth itself, not merely from the decay of organic matter at the surface, but from great depths, as for example in hot springs, so we may conceive the absolute amount of carbonic acid and ammonia on the surface of the earth and in the atmosphere to be somewhat greater now than some thousand years ago. If not, then the increase of animal and vegetable life in one part of the globe must necessarily cause a diminution of one or both in some other part, since, at all events, the atmosphere becomes neither richer nor poorer in carbonic acid and ammonia. Should an addition of these substances be made, they would instantly be appropriated by the vegetable kingdom, and converted into food for animals, of which an additional number would soon be produced by the increased supply of food; and thus the aggregate amount of animal and vegetable life might be increased, while the composition of the atmosphere remained unchanged, the vegetable world exactly balancing the animal, because each produces the food of the other, as the necessary result of its own existence.

Such is a very brief and general sketch of the chemistry of animal and vegetable life, as far as we are at all acquainted with it. It is only within a very short time that this department of science has been properly cultivated, but the results already obtained are most important and highly encouraging. When we reflect that the processes by which carbonic acid, water, ammonia, and the salts of the soil are made to assume the forms, first of vegetable and then of animal tissues, as well as those by which these tissues are again resolved into the elements of which they were formed, are, and must be, purely chemical processes of combination and decomposition, governed by the laws of chemistry as ascertained by observation and experiment, but modified by the vital force, it is easy to see that from the assiduous study of the chemical changes going on in plants and animals, in health and in disease, we may confidently expect the most beneficial results. All that has hitherto been done has only pointed out the path to be followed in order to obtain valuable and permanent results. But enough has been done to satisfy all who are acquainted with the actual state of physiology that, henceforth, it is chiefly to chemistry that we must look for the extension and improvoment of physiological science. Already a knowledge of chemistry is admitted to be indispensable to the physiologist, and before long this opinion will be so far acted on that no one who is not well versed in chemistry will venture to write on physiological subjects.

ADDENDA.

To page 173.

d. Ferric Acid. $FeO_3 = 52{\cdot}039$. Recent researches have established the existence of this compound, which corresponds to Manganic Acid. It is very easily decomposed, and is hardly known in a separate state. Ferrate of potash may be obtained in solution by igniting oxide of iron with nitre, or by passing chlorine through aqua potassa in which peroxide of iron is suspended. The solution has a very fine and intense purple colour, which, however, is not very permanent.

To page 398.

7. *Salicylate of oxide of methyle,* $MtO, SaO = C_{16} H_8 O_6$, is found, nearly pure, in the oil obtained by distilling with water the flowers of *Gaultheria procumbens*, a plant found abundantly in New Jersey. This oil is most remarkable as containing two compounds, salicylic acid and oxide of methyle, neither of which was previously known except as a product of decomposition of organic substances by artificial means.

The oil is very fragrant. When acted on by nitric acid, the salicylic acid is first converted into nitrosalicylic or anilic (indigotic) acid, and the anilate of oxide of methyle is obtained in crystals. The further action of nitric acid produces nitropicric acid.

When the oil of gaultheria is added to an excess of solution of potash, scaly crystals are formed, which are a compound of the oil with potash, and from which acids separate the oil unchanged. But if heated with the potash, hydrated oxide of methyle is given off, and salicylate of potash is left, from which acids separate pure salicylic acid.

Salicylamide. When the oil is left for a few days in contact with 6 times its bulk of strong aqua ammoniæ, it is entirely although slowly dissolved, and the solution leaves, on evaporation, a mass of brown crystals of a peculiar aromatic odour. By distillation, this mass yields colourless prismatic crystals of a new compound, which is found to be *salicylamide* ($C_{14} H_5 O_5, NH_3$)

$-HO = C_{14}H_7NO_4$. This compound is isomeric (or polymeric) with protonitrobenzoene (see p. 453), and with anthranilic acid (see p. 474); but when distilled with lime or baryta, it does not yield aniline, as both these compounds do, but is resolved into carbolic acid, ammonia, and a carbo-hydrogen.

When the oil of gaultheria is made to drop on red-hot baryta, it is resolved into carbonic acid and anisole, $C_{16}H_8O_6 + 2\,BaO = 2\,(BaO, CO_2) + C_{14}H_8O_2$. It would appear that the formula of anisole, given at p. 429, contains 1 eq. of hydrogen too little, and that the formula now given, namely, $C_{14}H_8O_2$, is the correct one, according to the most recent experiments.

To page 545.

Taurine. As mentioned in the Preface, Professor Redtenbacher has found taurine to contain 26 per cent. of sulphur. This remarkable fact has only been communicated generally, and without details, in a letter from Liebig to Pelouze, recently read to the Academy of Sciences in Paris. I have just tried the experiment (1st June, 1845), and I find that, when taurine is deflagrated with nitre, and the heated mass dissolved in water and neutralised with an acid, nitrate of baryta causes a very copious precipitate of sulphate. We may, therefore, assume the fact as proved; and in that case, all the now prevalent views of the bile, of its nature, its formation, possibly of its function, and of its relation to the body and the food, must undergo very serious modifications. The observation of Redtenbacher will probably turn out, in its consequences, one of the most important yet made in Animal Chemistry; and it cannot be doubted that, although our views must be changed in many points in consequence of it, our knowledge will be extended and rendered more precise, and more capable of direct application to physiology and pathology.

ERRATA IN PART I.

P. 84, l. 19, *for* " the sea-plant " *read* " sea-plants.'
P. 90, l. 13, *after* "air" *insert* " or."
P. 97, l. 12 *from bottom, for* " Pelouge " *read* " Pelouze."
P. 122, l. 21, *for* " C_6 N " *read* " C_2 N."
P. 136, l. 21, *for* " sulphates " *read* " sulphurets."
P. 142, l. 27, *for* " $KO, CO_2 + C = K + 3CO$ " *read* " $KO, CO_2 + C_2 = K + 3CO$.
P. 164, l. 37, *for* " yttrotartalite " *read* " yttrotantalite."
P. 165, l. 19, *for* " Acid " *read* " Aid."
P. 185, l. 1, *for* " Order 3 " *read* " Order 2."
P. 216, l. 15, *for* " Pt O " *read* " Pt O_2."

ERRATA IN PART II.

P. 266, l. 7 *from bottom, for* " $C_8 H_4 O_7, H_2$" *read* " $C_8 H_4 O_{12}, H_2$."
P. 266, l. 8 *from bottom, for* " $C_8 H_4 O_5$, 2HO, *read* $C_8 H_4 O_{101}$, 2HO.
P. 378, l. 6, *for* " perixide *read* " periodide."
P. 411, l. 1, *for* " $C_{12} H_4 O_{10}$" *read* " $C_8 H_4 O_{10}$."
P. 412, l. 9, *for* " $C_{12} H_6 O_5$" *read* " $C_{12} H_6 O_{15}$."
P. 481, headline, *for* " Nibotine " *read* " Nicotine."
P. 555, l. 11 *from bottom, for* " homatosine," *read* " hematosine."

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